NOMENCLATURE

Preparations are listed under the names which are used commonly for the compounds. For the convenience of those who wish to make a complete survey of the literature on any preparation, the *Chemical Abstracts* **indexing name** for each compound is given as a subtitle when that name differs from the title of the preparation.

NOTICE TO SUBMITTERS OF PREPARATIONS

Organic Syntheses invites the submission of preparations of compounds which are of general interest or which illustrate useful synthetic methods. Preparations are welcomed particularly from those who have had occasion to work out the optimum conditions of preparation. The directions should be written in the style employed in the latest volume of *Organic Syntheses*. A copy of the current style sheet will be sent to those who request it. Full details for all steps in the procedures should be included, and the range of yields should be reported rather than the maximum yield obtainable. Wherever possible the melting point, the boiling range at various pressures, and the refractive index of each product should be given. The method of preparation or source of compounds used should be recorded as well as criteria of purity. Two copies of the directions should be sent to the Secretary. Additions, corrections, and improvements to previously published preparations are likewise welcomed.

β-ALANINE

$$2NH_2CH_2CH_2CN + Ba(OH)_2 + 2H_2O \rightarrow (NH_2CH_2CH_2COO)_2Ba + 2NH_3$$

$$(NH_2CH_2CH_2COO)_2Ba + CO_2 + H_2O \rightarrow 2NH_2CH_2CH_2COOH + BaCO_3$$

Submitted by Jared H. Ford.
Checked by Homer Adkins and James M. Caffrey.

1. Procedure

In a 2-l. three-necked flask equipped with a mechanical stirrer, a thermometer, and a dropping funnel is placed 185 g. (0.55 mole) of technical barium hydroxide octahydrate. The flask is heated on a steam bath in a hood. When the barium hydroxide has dissolved in its water of crystallization, the stirrer is started and 70.1 g. (1.00 mole) of β-aminopropionitrile (p. 3) is added dropwise over a period of 40 minutes. The temperature is maintained at 90–95° during the addition and for 40 minutes thereafter. Forty grams of asbestos filter aid (Note 1) and 1 l. of hot water are added, and the mixture is saturated with carbon dioxide (Note 2) while the temperature is held at 85–90°. The mixture is filtered with suction, the precipitate is returned to the flask with 500 ml. of hot water, and the mixture is heated and stirred for 20 minutes. After the barium carbonate has been filtered the washing procedure is again repeated with a second 500 ml. of hot water. The combined filtrates and washings are concentrated under reduced pressure on the steam bath (Note 3) until solid material separates. To the residue are added 200 ml. of hot water and 0.5 g. of decolorizing carbon (Note 4). The resulting solution is warmed on the steam bath for a few minutes and then filtered into a weighed 500-ml. Erlenmeyer flask. The flask

is heated on a steam bath, and a jet of clean compressed air is directed at the surface of the solution. When the total weight of the solution is 130 g., it is cooled to 15–20° and diluted slowly with 400 ml. of methanol. After the solution has stood for several hours in the refrigerator, the product is filtered with suction and washed with two 100-ml. portions of methanol. The yield of β-alanine melting at 197–198° (dec.) is 75–80 g. (85–90%).

2. Notes

1. Standard Super-Cel (Johns-Manville, Inc.) was used.
2. Either carbon dioxide gas or Dry Ice may be used, and the saturation may be completed in 15–20 minutes by either method. The *p*H of the saturated solution is about 8–9 when tested with a universal indicator paper, such as Alkacid or Hydrion.
3. The submitter used a special apparatus suitable for the rapid evaporation of water under reduced pressure. The checkers used standard flasks.
4. The solution is nearly colorless at this point, but the carbon aids in the removal of finely divided insoluble material.

3. Methods of Preparation

β-Alanine has been prepared by the catalytic reduction of cyanoacetic esters [1] or salts; [2] by heating acrylonitrile,[3] β-aminopropionitrile,[4] *bis*-(β-cyanoethyl)-amine,[5] β-hydroxypropionitrile,[6] β-alkoxypropionitriles,[7] *bis*-(β-cyanoethyl) ether,[8] or *bis*-(β-cyanoethyl) sulfide [8] with aqueous ammonia at 150–225°; by the hydrolysis of β-aminopropionitrile with concentrated hydrochloric acid and subsequent removal of the acid with anion exchange resins.[9] The method as described above has been published.[10] Additional references to methods of preparation are given in connection with a procedure for the making of β-alanine from succinimide through the action of potassium hypobromite.[11]

[1] Schaaf and Pickel, U. S. pat. 2,365,295 [*C. A.*, **39**, 4626 (1945)].
[2] Ruggli and Businger, U. S. pat. 2,367,436 [*C. A.*, **39**, 3012 (1945)].

[3] Carlson and Hotchkiss, U. S. pat. 2,335,997 [*C. A.*, **38**, 2972 (1944)].
[4] Carlson, U. S. pat. 2,336,067 [*C. A.*, **38**, 2971 (1944)].
[5] Kirk, U. S. pat. 2,334,163 [*C. A.*, **38**, 2667 (1944)].
[6] Kirk and Paden, U. S. pat. 2,364,538 [*C. A.*, **39**, 3556 (1945)].
[7] Paden and Kirk, U. S. pat. 2,335,605 [*C. A.*, **38**, 2970 (1944)].
[8] Dean, U. S. pat. 2,335,653 [*C. A.*, **38**, 2970 (1944)].
[9] Buc, Ford, and Wise, *J. Am. Chem. Soc.*, **67**, 92 (1945).
[10] Ford, *J. Am. Chem. Soc.*, **67**, 876 (1945).
[11] *Org. Syntheses* Coll. Vol. **2**, 20 (1943).

β-AMINOPROPIONITRILE and *bis*-(β-CYANOETHYL)-AMINE

(Propionitrile, β-amino-, and **propionitrile, β,β′-iminodi-)**

$$NH_3 + CH_2{=}CH{-}CN \rightarrow NH_2CH_2CH_2CN$$

$$NH_2CH_2CH_2CN + CH_2{=}CH{-}CN \rightarrow NH(CH_2CH_2CN)_2$$

Submitted by SAUL R. BUC.
Checked by HOMER ADKINS and JAMES M. CAFFREY.

1. Procedure

Acrylonitrile is a poisonous compound. All steps in the procedure up to the distillation of the products should be carried out in a hood.

The reactions are carried out in 1-l. heavy-walled bottles provided with rubber stoppers which must be wired securely in place (Note 1). In each of four bottles are placed 400 ml. of concentrated ammonium hydroxide (28–30% ammonia) and 100 ml. (80 g., 1.5 moles) of cold acrylonitrile (Note 2). The rubber stoppers are immediately wired in place (Note 3). Each bottle is then shaken intermittently until after about 5 minutes the reaction mixture becomes homogeneous. Thereupon, the bottle, wrapped in a towel, is immediately set away under a hood (Note 4).

The reaction mixtures are allowed to stand a few hours or overnight and then are transferred to a 3-l. flask. The water and ammonia are distilled under reduced pressure as rapidly as

possible until the boiling point is about 50°/20 mm. (Note 5). The higher-boiling products (395 g.) are then transferred to a 1-l. Claisen flask and fractionated under reduced pressure.

The crude primary amine (138–149 g.) is distilled over the range 75–110°/21 mm. (Note 6), and the crude secondary amine (213–226 g.) in the range 130–150°/1 mm. The primary amine, b.p. 79–81°/16 mm. or 87–89°/20 mm. (n_D^{20} 1.3496), after refractionation, is obtained in a yield of 130–140 g. (31–33%) (Note 7). The secondary amine, b.p. 134–135°/1 mm. (n_D^{20} 1.4640), is obtained in a yield of about 210 g. (57%).

2. Notes

1. The 1-l. centrifuge bottles (Corning No. 1280) carrying No. 6 rubber stoppers, as used for catalytic hydrogenation, are suitable for carrying out reactions under pressures up to at least 3 atmospheres. The submitter used a heavy, selected 2-l. round-bottomed flask instead of the four bottles specified in the procedure above.

2. The acrylonitrile should be free of polymer. If there is uncertainty as to its quality, the acrylonitrile should be redistilled.

3. The temperature of the mixture does not rise during the period of solution of the acrylonitrile in the ammonium hydroxide. However, almost immediately thereafter the temperature of the solution begins to rise slowly, reaching a value of about 65° after an interval of perhaps 10 minutes. There is no significant rise in pressure within the bottle until the temperature of the reaction mixture begins to rise. The maximum pressure reached is apparently less than 2 atm.

4. The checkers placed the wrapped bottles within a 10-gal. crock located under a hood. There is no danger that the bottles will be broken by the pressure developed. However, if a stopper is not firmly held, it may be pushed out, in which event a portion of the reaction mixture will foam out of the bottle.

5. The submitter used a special apparatus suitable for the rapid evaporation of water under reduced pressure. The checkers used standard flasks. Better yields result from the rapid removal of water.

6. It is not necessary to purify the crude primary amine by redistillation if it is to be used immediately for the preparation of β-alanine. However, the moist nitrile is not stable in storage, pressure being developed in a container stored at room temperature.

7. Yields of 60–80% of the primary amine [1] have been obtained by introducing the acrylonitrile below the surface of the aqueous ammonia preheated to 110° in a steel reactor suitable for pressure reactions.

3. Methods of Preparation

β-Aminopropionitrile and *bis*-(β-cyanoethyl)-amine have been made by the addition of anhydrous [2,3] or aqueous [4] ammonia to acrylonitrile.

[1] Ford, Buc, and Greiner, *J. Am. Chem. Soc.*, **69**, 844 (1947).
[2] Hoffmann and Jacobi, U. S. pat. 1,992,615 [*C. A.*, **29**, 2548 (1935).
[3] Whitmore, Mosher, Adams, Taylor, Chapin, Weisel, and Yanko, *J. Am. Chem. Soc.*, **66**, 725 (1944).
[4] Buc, Ford, and Wise, *J. Am. Chem. Soc.*, **67**, 92 (1945).

BENZALACETONE DIBROMIDE

(2-Butanone, 3,4-dibromo-4-phenyl-)

$$C_6H_5CH{=}CHCOCH_3 + Br_2 \rightarrow C_6H_5CHBrCHBrCOCH_3$$

Submitted by Norman H. Cromwell and Richard Benson.
Checked by R. L. Shriner and William O. Foye.

1. Procedure

In a 1-l. three-necked round-bottomed flask fitted with an efficient mechanical stirrer, a thermometer, and a 125-ml. dropping funnel are placed 100 g. (0.68 mole) of pure, redistilled benzal-

acetone [1] and 300 ml. of carbon tetrachloride. The reaction flask is immersed in an ice-water bath to maintain the reaction mixture between 10° and 20°. With stirring, a cooled solution of 109.5 g. (34.2 ml., 0.68 mole) of bromine in 60 ml. of carbon tetrachloride is run through the dropping funnel as rapidly as the color is destroyed (Note 1). During this addition the reaction flask should be shielded from direct sunlight (Note 2).

After all the bromine has been added, stirring is continued for 4 to 5 minutes longer and the dibromide is collected by filtration on an 11-cm. Büchner funnel, using suction. The product is washed with 100 ml. of warm 75% ethanol (Note 3). The crude product is purified by dissolving in the minimum amount of boiling methanol (800–1000 ml.) and cooling the solution in an ice bath for 4 hours. The product is collected by filtration and dried in a vacuum desiccator in the absence of light for 24 hours. The yield amounts to 110–120 g. (52–57%) of white needles which melt at 124–125° (Note 4).

2. Notes

1. Until a considerable amount of the dibromide has precipitated the bromine solution may be run into the reaction mixture as fast as the color is discharged, within the temperature limits of 10–20°. As the mixture becomes thick with the precipitated bromide it is necessary to reduce the speed of the addition of the bromine solution considerably.

2. Strong sunlight seems to favor the substitution of the available α-hydrogen as evidenced by the strong evolution of hydrogen bromide.

3. If the crude product is dried it is found to melt at 114–117° and to weigh 138–144 g. This is probably a mixture of the two racemic forms.

4. Evaporation and subsequent cooling of the filtrate give a second crop of white crystals, about 15 g., melting at 112–115°. This may be the lower-melting racemate.

3. Methods of Preparation

Benzalacetone dibromide has been prepared by the addition of bromine to a solution of benzalacetone in chloroform,[2] in carbon disulfide,[3] and in carbon tetrachloride.[4]

[1] *Org. Syntheses* Coll. Vol. **1**, 77 (1941).
[2] Claisen and Claparede, *Ber.*, **14**, 2463 (1881).
[3] Watson, *J. Chem. Soc.*, **85**, 464 (1904).
[4] Cromwell, *J. Am. Chem. Soc.*, **62**, 3471 (1940).

BIALLYL

(1,5-Hexadiene)

$$2CH_2{=}CHCH_2Cl + Mg \rightarrow CH_2{=}CH(CH_2)_2CH{=}CH_2 + MgCl_2$$

Submitted by Amos Turk and Henry Chanan.
Checked by Arthur C. Cope and Frank S. Fawcett.

1. Procedure

In a 5-l. three-necked flask fitted with a mercury-sealed stirrer (Note 1), dropping funnel, and an efficient reflux condenser protected by a calcium chloride drying tube is placed 82 g. (3.5 gram atoms) of magnesium turnings. A solution of 459 g. (6 moles) of dry, freshly distilled allyl chloride in 2.4 l. of anhydrous ether is added to the flask through the dropping funnel in the following manner: A 100- to 200-ml. portion of the solution and a small crystal of iodine are added, and the mixture is warmed, if necessary, until the reaction starts. The remainder of the solution is added with stirring and cooling in an ice bath as rapidly as possible without loss of material through the condenser (Note 2). By sponging the upper part of the flask with ice water from the cooling bath, the addition can be completed in 1–1.5 hours. When the addition is complete, the thick slurry is allowed to stand at room temperature for 5 hours with stirring for as much

of that period as is practicable (Note 1). The flask is again cooled in an ice bath, and a cold 5% solution of hydrochloric acid is added through the dropping funnel until the evolution of heat has practically ceased (Note 2) and the magnesium chloride is in solution. The mechanical stirrer is started again when the mixture becomes sufficiently fluid (Note 1).

The contents of the flask are transferred to a separatory funnel; the ether layer is separated and distilled without washing or drying through a small packed column (Note 3) until the distillation temperature begins to rise (38–40°). The residue is transferred to a separatory funnel, washed with two 500-ml. portions of water, dried over 10 g. of calcium chloride, and fractionated through the small packed column. After distillation of ether and some allyl chloride (b.p. 45°) biallyl is collected as a colorless liquid in a yield of 135–160 g. (55–65%), b.p. 59–60°/760 mm.; n_D^{20} 1.4040; n_D^{25} 1.4012.

2. Notes

1. Efficient stirring is essential during the early part of the reaction. The submitters used a double-loop-type Hershberg wire (Nichrome, Chromel, or tantalum) stirrer [1] and a motor [2] powerful enough to stir the mixture during the entire preparation. The checkers used the simpler Hershberg wire (No. 16 B and S gauge Chromel or stainless steel) stirrer [3] and an ordinary good laboratory motor. Although the slurry became so thick that it could not be stirred with this equipment, the yield of pure biallyl obtained equaled that reported by the submitters.

2. Care must be taken to avoid loss of material (and reduction in yield) through evaporation of allyl chloride or biallyl, both of which are very volatile.

3. A simple total-condensation, partial take-off column with a 2.2 by 25 cm. section packed with 3/32-in. single-turn glass helices was used with a reflux ratio of 7 or 8 to 1.

3. Methods of Preparation

This procedure is a modification of one described by Cortese.[4] Allyl chloride is employed rather than allyl bromide because of its low cost. Biallyl has been prepared by the action of sodium [5] or aluminum [6] on allyl iodide; from allyl mercuric iodide by dry distillation [7] or by the action of potassium cyanide solution;[8] and by the action of magnesium on allyl bromide,[4,9] on allyl chloride,[4,10] on allyl iodide,[11] or on 1,2,3-tribromopropane.[12]

1 *Org. Syntheses* Coll. Vol. **2**, 117 (1943).
2 Hershberg, *Ind. Eng. Chem., Anal. Ed.*, **12**, 293 (1940).
3 Hershberg, *Ind. Eng. Chem., Anal. Ed.*, **8**, 313 (1936).
4 Cortese, *J. Am. Chem. Soc.*, **51**, 2266 (1929).
5 Berthelot and Luca, *Ann. chim. phys.*, (3), **48**, 294 (1856).
6 Domanitzkii, *J. Russ. Phys.-Chem. Soc.*, **46**, 1078 (1914) [*C. A.*, **9**, 1899 (1915)].
7 Linnemann, *Ann.*, **140**, 180 (1866).
8 Oppenheim, *Ber.*, **4**, 670 (1871).
9 Lespieau, *Ann. chim. phys.*, (8), **27**, 149 (1912); Gilman and McGlumphy, *Bull. soc. chim.*, **43**, 1322 (1928).
10 Henne, Chanan, and Turk, *J. Am. Chem. Soc.*, **63**, 3474 (1941).
11 Meisenheimer and Casper, *Ber.*, **54**, 1655 (1921).
12 Krestinskii, *J. Russ. Phys.-Chem. Soc.*, **58**, 1078 (1926) [*C. A.*, **22**, 1324 (1928)].

α-BROMOBENZALACETONE

(3-Buten-2-one, 3-bromo-4-phenyl-)

$$C_6H_5CHBrCHBrCOCH_3 + CH_3CO_2Na \rightarrow C_6H_5CH{=}CBrCOCH_3 + CH_3CO_2H + NaBr$$

Submitted by Norman H. Cromwell, Donald J. Cram, and Chas. E. Harris.
Checked by R. L. Shriner and William O. Foye.

1. Procedure

Precautions must be taken to avoid contact with α-bromobenzalacetone since it is a skin irritant (Note 1).

In a 500-ml. round-bottomed flask fitted with a reflux condenser are placed 100 g. (0.33 mole) of benzalacetone dibromide

(p. 5), 30 g. (0.37 mole) of anhydrous sodium acetate, and 250 ml. of 95% ethanol, and the mixture is refluxed vigorously for 4 hours in the absence of direct sunlight. The precipitate of sodium bromide is removed by filtration, and the alcohol is removed from the filtrate by distillation under reduced pressure (Note 2). The residual salt-oil mixture is extracted with two 50-ml. portions of ether, and the ether solution is transferred to a 250-ml. separatory funnel (Caution! Note 1).

The ether solution is washed thoroughly six times with 25-ml. portions of saturated sodium chloride solution and twice with 25-ml. portions of 5% sodium bicarbonate solution (Note 3). The ether layer is allowed to dry over anhydrous sodium sulfate at room temperature for 24 hours. The ether is removed by distillation, and the residual oil is distilled from a Claisen flask under reduced pressure, using an oil bath. A yield of 47–54 g. (64–73%) of a pale yellow oil, boiling at 114–117°/1 mm. (Note 4), is obtained. On cooling, the oil crystallizes; m.p. 30–31°. The product is stored in a dark bottle in the ice chest (Notes 5 and 6).

2. Notes

1. α-Bromobenzalacetone or its solutions cause the formation of red spots on the skin. After several days these form large red blisters that are painful and take several days to heal. The affected parts should be treated with a mixture of peanut-oil and glycerol containing a little ammonia.

2. The reduced pressure produced by a water pump is satisfactory. The flask is warmed with a hot water bath (40–50°).

3. It is necessary that the product be entirely free from acetic acid before it is distilled in order to obtain the yields stated.

4. Boiling points at other pressures are: 136–138°/4 mm.; 150–151°/10 mm.

5. When stored in this manner the product is quite stable and darkens only slightly after 9 months.

6. The analogous α-bromobenzalacetophenone may be prepared by a similar procedure. In a 1-l. three-necked round-bottomed flask fitted with a mercury-sealed stirrer and a reflux

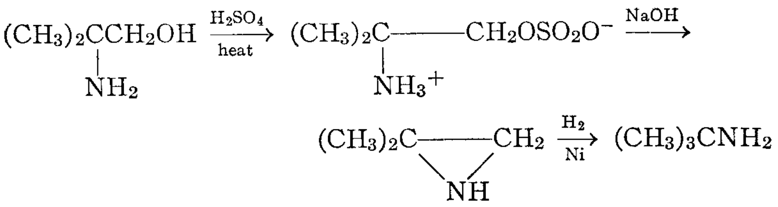
condenser are placed 150 g. (0.41 mole) of benzalacetophenone dibromide,[1] 41 g. (0.50 mole) of anhydrous sodium acetate, and 250 ml. of 95% ethyl alcohol. The mixture is stirred and refluxed for 5 hours and then worked up in the same manner as described above for α-bromobenzalacetone. Distillation gives a yield of 100–110 g. (85–94%) of a pale yellow oil, boiling at 170–173°/1 mm. On cooling, the oil crystallizes and melts at 42–44°. This product should also be stored in a dark bottle in the ice chest, but it is more stable and darkens less on standing than the analogous α-bromobenzalacetone. This product is less irritating to the skin than α-bromobenzalacetone (Note 1).

3. Methods of Preparation

α-Bromobenzalacetone has been prepared from benzalacetone dibromide by heating with alcoholic potassium hydroxide[2] or with sodium acetate[3] solutions. α-Bromobenzalacetophenone is prepared by a similar procedure from benzalacetophenone dibromide.[4]

[1] *Org. Syntheses* Coll. Vol. **1**, 205 (1941).
[2] Watson, *J. Chem. Soc.*, **85**, 464 (1904).
[3] Cromwell and Cram, *J. Am. Chem. Soc.*, **65**, 305 (1943).
[4] Wislicenus, *Ann.*, **308**, 226 (1899); Cromwell, *J. Am. Chem. Soc.*, **62**, 2899 (1940).

tert.-BUTYLAMINE



Submitted by Kenneth N. Campbell, Armiger H. Sommers, and Barbara K. Campbell.
Checked by Nathan L. Drake and Sidney Melamed.

1. Procedure

A. *2,2-Dimethylethylenimine.* A cold mixture of 110 g. (60 ml., 1.06 moles) of concentrated sulfuric acid and 200 ml. of water is added in portions, with shaking, to a solution of 100 g. (107 ml., 1.12 moles) of 2-amino-2-methyl-1-propanol in 200 ml. of water contained in a 1-l. round-bottomed flask (Note 1). The flask is fitted with a thermometer extending into the liquid and a short still head carrying a downward condenser.

Water is distilled from the mixture at atmospheric pressure until the temperature of the solution reaches 115° (Notes 2 and 3) whereupon the liquid is transferred to a 500-ml. round-bottomed flask. This flask is connected to the distillation apparatus used previously except that the thermometer is replaced by a capillary tube. Distillation is then continued under the reduced pressure obtainable from a water aspirator. The bath temperature is raised to 175° over a period of about an hour and is held there until the mixture solidifies (usually 30–60 minutes longer), and for 1 hour thereafter. The flask is cooled and broken to remove the product.

The brown solid from the above operations is ground in a mortar and placed in a 500-ml. distilling flask equipped with a downward condenser and a receiver. A cold solution of 100 g.

(2.5 moles) of technical sodium hydroxide in 150 ml. of water is added to the solid in the flask, and heat is applied by means of an oil bath whose temperature is slowly raised to 125°. From 70 to 75 g. of distillate is collected; the head temperature ranges from about 70° to 101° (Note 2). The distillate is cooled in ice and saturated with technical potassium hydroxide; the organic layer which forms is separated and dried over potassium hydroxide pellets in a refrigerator for about 15 hours.

The organic layer is separated from the drying agent and distilled from a few fresh pellets of potassium hydroxide through a column of the Whitmore-Fenske type. After a 3- to 5-g. fore-run, the product distils at 71–72°; the yield is 36–41 g. (45–51%) (Notes 4 and 5).

B. *tert.-Butylamine.* A hydrogenation bomb or bottle (Note 6) is charged with 100 ml. of purified dioxane,[1] 35.5 g. (0.5 mole) of freshly distilled 2,2-dimethylethylenimine, and about 9 g. (alcohol-wet weight) of Raney nickel.[2] The apparatus is filled with hydrogen, warmed to 60°, and shaken until hydrogenation is complete (Note 7). The contents of the bomb are removed and filtered to separate the catalyst which is washed on the funnel with a little dioxane.

The filtrates from two such runs are combined and distilled through a Whitmore-Fenske column of 10–15 theoretical plates at a 5:1 reflux ratio. The yield of *tert.*-butylamine is 55–60 g. (75–82%); the product boils at 44–44.5°, and its refractive index is n_D^{20} 1.3770 (Note 8).

2. Notes

1. The 2-amino-2-methyl-1-propanol used was the Practical grade obtained from the Eastman Kodak Company. This aminoalcohol can also be secured from the Commercial Solvents Corporation.

2. A Glass-Col heater may conveniently be substituted for the oil bath specified.

3. Approximately 285 ml. of water must be collected before the temperature of the reaction mixture reaches 115°.

4. 2,2-Dimethylethylenimine polymerizes on standing; the product should be hydrogenated within a few hours after preparation.

5. The checkers have followed the same procedure successfully using tenfold quantities; the yield of the imine was 42%.

6. The hydrogenation can be carried out equally well in metal or glass equipment. If a hydrogenator of the Parr low-pressure type is used, the bottle can be wound for electrical heating. Five turns of 24-gauge asbestos-covered Nichrome or Chromel A wire is satisfactory for the heating element. In use, current is supplied from a variable transformer, and the voltage necessary to heat the contents of the bottle to 60° is determined by experiment. The checkers used hydrogenation equipment supplied by the American Instrument Company.

7. If the hydrogenation is carried out in a Parr hydrogenation apparatus at 40–60 lb. pressure, about 2 hours is required to complete the hydrogenation as described. The low boiling point of the ethylenimine makes it impossible to remove the air from the bottle by evacuation in the usual way prior to hydrogenation. Instead the bottle is filled with hydrogen to 15–20 lb. pressure, the pressure is released, and the process repeated.

8. The checkers used high-pressure equipment and found that the hydrogenation of 336 g. of 2,2-dimethylethylenimine in 250 ml. of purified dioxane in the presence of 3 teaspoonfuls of Raney nickel under 3000 lb. hydrogen pressure was complete in 10–15 minutes; the temperature rise during the hydrogenation was about 50°. The yield of product was 283 g. (82%).

3. Methods of Preparation

2,2-Dimethylethylenimine has been prepared by the dehydration of 2-amino-2-methyl-1-propanol.[3] The method described here is essentially that of Cairns.[3]

tert.-Butylamine has been prepared by the Hofmann rearrangement of trimethylacetamide,[4] by the action of *tert.*-butylmagnesium chloride on monochloramine[5] or O-methylhydroxylamine,[6] by the reduction of *tert.*-butylhydrazide,[7] and from *tert.*-butylurea.[8] It has been prepared from 2,2-dimethylethylenimine by low-pressure hydrogenation[9] and by high-pressure hydrogenation.[10]

[1] Fieser, *Experiments in Organic Chemistry*, 2nd ed., p. 369, D. C. Heath and Co., 1941. See also Hess and Frahm, *Ber.*, **71**, 2627 (1938).
[2] *Org. Syntheses*, **21**, 15 (1941).
[3] Cairns, *J. Am. Chem. Soc.*, **63**, 871 (1941).
[4] van Erp, *Rec. trav. chim.*, **14**, 16 (1895).
[5] Coleman and Yager, *J. Am. Chem. Soc.*, **51**, 567 (1929).
[6] Sheverdina and Kocheshkov, *J. Gen. Chem. U.S.S.R.*, **8**, 1825 (1938) [*C. A.*, **33**, 5804 (1939)].
[7] Klages et al., *Ann.*, **547**, 1 (1941).
[8] Smith and Emerson, *J. Am. Chem. Soc.*, **67**, 1862 (1945).
[9] Campbell, Sommers, and Campbell, *J. Am. Chem. Soc.*, **68**, 140 (1946).
[10] Karabinos and Serijan, *J. Am. Chem. Soc.*, **67**, 1856 (1945).

CARBOXYMETHOXYLAMINE HEMIHYDROCHLORIDE

(Acetic acid, aminoöxy-, hydrochloride)

$$(CH_3)_2C{=}NONa + BrCH_2CO_2Na \rightarrow (CH_3)_2C{=}NOCH_2CO_2Na + NaBr$$

$$(CH_3)_2C{=}NOCH_2CO_2Na + HCl \rightarrow (CH_3)_2C{=}NOCH_2CO_2H + NaCl$$

$$2(CH_3)_2C{=}NOCH_2CO_2H + 2H_2O + HCl \rightarrow (H_2NOCH_2CO_2H)_2HCl + 2(CH_3)_2CO$$

Submitted by H. S. Anker and H. T. Clarke.
Checked by H. R. Snyder and Peter Kovacic.

1. Procedure

A. *Acetone carboxymethoxime.* A mixture of 612 g. (4.4 moles) of bromoacetic acid (Note 1) and 500 g. of crushed ice is chilled in an ice-salt bath and made distinctly alkaline to litmus with sodium hydroxide (about 440 g. of a 40% solution). During the neutralization an additional 500 g. of ice is added. To the solution are then added 292 g. (4.0 moles) of acetoxime[1] and 440 g. of 40% sodium hydroxide (4.4 moles), the temperature being held

below 20° during the addition of the alkali. The mixture is then allowed to flow dropwise, during 3–4 hours, through the inner tube of a steam-heated Liebig condenser (jacket 75 cm. long; inner tube 10-mm. diameter; angle of inclination about 20°) into a 5-l. round-bottomed flask cooled with running water (Note 2). The resulting solution is extracted three times with 500-ml. quantities of freshly distilled peroxide-free ether (Note 3), and the aqueous solution is then cooled and made strongly acid by the addition of 500 ml. of concentrated hydrochloric acid (6 moles). During the acidification the temperature should not rise above 15°. The solution is saturated with sodium chloride and immediately extracted with six successive 1500-ml. portions of peroxide-free ether. The ether is distilled from the combined ethereal extracts, and the residue, consisting of the crude acetone carboxymethoxime (333–345 g.), is used for the next step. The acetone carboxymethoxime may be purified by distillation under reduced pressure, the fraction boiling at 95–97°/1 mm. (Note 4) being collected (Note 5). The yield is 300 g. (57%) of a colorless product melting at 76°.

B. *Carboxymethoxylamine hemihydrochloride.* The crude acetone carboxymethoxime is dissolved in about twice its weight of benzene; the solution is filtered and freed of benzene by distillation under reduced pressure from a steam bath. To a solution of 200 g. (1.52 moles) of the residue in 1 l. of water, in a 5-l. flask, are added 2 mg. of hydroquinone and 1 l. of concentrated hydrochloric acid. The flask is connected with a condenser, and steam is passed through the solution until acetone no longer comes over (30–40 minutes). The solution is concentrated under reduced pressure to a volume of 180–220 ml., and 400 ml. of isopropyl alcohol is added. The solution is then stored for 12 hours in the icebox, and the crystals which separate are collected on a Büchner funnel and washed with cold isopropyl alcohol. Further crops are obtained by concentrating the mother liquors and adding isopropyl alcohol. The crude product (120–135 g.) may be recrystallized (Note 6) with very little loss by dissolving it in twice its weight of warm (50°) water (Note 7), adding 2 volumes of isopropyl alcohol, and again chilling in an icebox.

Further small quantities can be recovered from the mother liquors by systematic repetition of the process described. The yield is 110–120 g. (66–72%) of white crystals which melt with decomposition at 152–153° (Note 8).

2. Notes

1. Chloroacetic acid gives a poorer yield (46–49%) of acetone carboxymethoxime, and the crude product is more difficult to purify.[2]

2. By this procedure, the reaction takes place in a few seconds, and the formation of by-products is minimized. If the solution of the reactants is heated in bulk, the reaction temperature cannot be controlled, and a lower yield is obtained of a dark product which, however, can be purified by distillation under reduced pressure.

3. The unchanged acetoxime extracted by the ether amounts to 14–24 g. (5–8%).

4. The temperature of the vapor, during distillation under apparently comparable conditions, may differ from run to run by as much as 20°. The temperature range of 95–97° is the lowest observed for 1-mm. pressure. Boiling ranges of 110–118°/1 mm. have been reported.

5. No carbonization and only slight formation of hydrogen cyanide, which occurs extensively during the distillation of preparations from chloroacetic acid,[2] are observed.

6. The use of decolorizing carbon should be avoided, as some brands appear to contain impurities which catalyze decomposition to ammonium chloride.

7. If the resulting aqueous solution is cooled to 0° before the addition of isopropyl alcohol, about one-third of the product crystallizes in very pure form.

8. The melting point depends on the rate at which the sample is heated. When the temperature is raised in the ordinary way the material melts (with evolution of gas) at 152–153°; when the bath is heated to 150° before the sample is inserted, the melting point is 159°. On the other hand, when a sample is held be-

tween 140° and 145° it melts after about 6 minutes. Decomposition evidently plays a large part in the matter.

3. Methods of Preparation

Carboxymethoxylamine (also called hydroxylamine-O-acetic acid), which is of value for the isolation of ketones,[3] has been prepared by the hydrolysis of ethylbenzhydroximinoacetic acid[4] and of ethyl benzohydroximinoacetate.[5] The present method is a modification of that described by Borek and Clarke.[2]

[1] *Org. Syntheses* Coll. Vol. **1**, 318 (1941).
[2] Borek and Clarke, *J. Am. Chem. Soc.*, **58**, 2020 (1936).
[3] Anchel and Schoenheimer, *J. Biol. Chem.*, **114**, 539 (1936).
[4] Werner, *Ber.*, **26**, 1567 (1893); Werner and Sonnenfeld, *Ber.*, **27**, 3350 (1894).
[5] Kitagawa and Takani, *J. Biochem. Japan*, **23**, 181 (1936).

DECAMETHYLENEDIAMINE

(1,10-Decanediamine)

$$\begin{array}{c} CN \\ | \\ (CH_2)_8 \\ | \\ CN \end{array} + 4H_2 \xrightarrow[(Ni)]{NH_3} \begin{array}{c} CH_2NH_2 \\ | \\ (CH_2)_8 \\ | \\ CH_2NH_2 \end{array}$$

Submitted by B. S. Biggs and W. S. Bishop.
Checked by C. F. H. Allen and John R. Byers, Jr.

1. Procedure

A high-pressure bomb of about 1.1-l. capacity is charged with 82 g. (0.50 mole) of sebaconitrile[1] and about 6 g. of Raney nickel catalyst[2] (Note 1) suspended in 25 ml. of 95% ethanol, using an additional 25 ml. of ethanol to rinse in the catalyst. The bomb is closed (Note 2), and about 68 g. (4 moles) of liquid ammonia is introduced from a tared, 5-lb. commercial cylinder (Note 3). Hydrogen is then admitted at tank pressure (1500 lb.), and the temperature is raised to 125°. The reaction starts at about 90°

and proceeds rapidly at 110–125°. When hydrogen is no longer absorbed (1–2 hours) the heater is shut off and the bomb allowed to cool. The hydrogen and ammonia are allowed to escape, and the contents of the bomb are rinsed out with two 100-ml. portions of 95% ethanol. The alcoholic solution is filtered quickly through a layer of decolorizing carbon (Note 4) to remove the catalyst and transferred to a 500-ml. Claisen flask having a modified side arm and connected by ground-glass joints to a receiver (Note 5). The alcohol is removed by distillation at atmospheric pressure, the receiver is changed, and the decamethylenediamine is distilled under reduced pressure. It boils at 143–146°/14 mm. (Note 6) and solidifies, on cooling, to a white solid, freezing point 60°. The yield is 68–69 g. (79–80%) (Notes 7, 8, and 9).

2. Notes

1. Raney nickel catalyst, already prepared and suspended in water, can be obtained from the Gilman Paint and Varnish Company, Chattanooga, Tennessee.

2. The safety disk should be made of steel, nickel, or other suitable material. It must not be of copper, which is readily attacked by ammonia under pressure.

3. The ammonia may be introduced by a number of methods. Suitable ones are given under α-phenylethylamine[3] and aminoacetal.[4] The amount of ammonia is not critical, but maximum yields are obtained when 6–8 moles is used per mole of dinitrile. The purpose of the ammonia is to suppress secondary amine formation.[5,6]

4. A 9-cm. Büchner funnel is used. The decolorizing carbon is deposited from a slurry in alcohol.

5. As decamethylenediamine combines with atmospheric carbon dioxide rapidly, any solutions left standing should be protected by a drying tube containing solid potassium hydroxide. When air is admitted to the apparatus at the end of the distillation it should be through such a tube.

6. Decamethylenediamine should not be allowed to solidify in a bottle or Erlenmeyer flask, since it will probably break such

a container. A tared round-bottomed flask less than half filled is advisable.

7. A dermatitis is induced in susceptible individuals by decamethylenediamine.

8. The submitters reported yields of 85–90% on runs four times this size.

9. Other boiling points are 139–140°/12 mm.; 126–127°/5 mm.

3. Methods of Preparation

Decamethylenediamine has been obtained by reduction of sebaconitrile either catalytically[5] or by sodium and alcohol.[7] It has also been obtained by hydrolysis of the condensation product from decamethylene iodide and phthalimide.[8]

[1] *Org. Syntheses*, **25**, 95 (1945).
[2] *Org. Syntheses*, **21**, 15 (1941).
[3] *Org. Syntheses*, **23**, 69 (1943).
[4] *Org. Syntheses*, **24**, 3 (1944).
[5] Clark, Brit. pat. 490,922 [*C. A.*, **33**, 993 (1939)].
[6] Schwoegler and Adkins, *J. Am. Chem. Soc.*, **61**, 3499 (1939).
[7] Phookan and Krafft, *Ber.*, **25**, 2253 (1892).
[8] von Braun, *Ber.*, **42**, 4551 (1909).

DIETHYLAMINOACETONITRILE

(Acetonitrile, diethylamino-)

$$(C_2H_5)_2NH + NaCN + CH_2O + NaHSO_3 \rightarrow (C_2H_5)_2NCH_2CN + Na_2SO_3 + H_2O$$

Submitted by C. F. H. ALLEN and J. A. VANALLAN.
Checked by CLIFF S. HAMILTON, A. F. HARRIS, and C. W. WINTER.

1. Procedure

This preparation should be carried out under a good hood since poisonous hydrogen cyanide may be evolved.

To a solution of 312 g. (3 moles) of sodium bisulfite in 750 ml. of water in a 3-l. beaker is added 225 ml. of a 37–40% formaldehyde solution, and the mixture is warmed to 60°. After cooling to 35°, 219 g. (309 ml., 3 moles) of diethylamine is added with hand stirring, and the mixture is allowed to stand for 2 hours. The beaker containing the reaction mixture is placed under a good hood, and to it is added a solution of 147 g. (3 moles) of sodium cyanide dissolved in 400 ml. of water with efficient stirring so that the two layers are thoroughly mixed. After 1.5 hours the upper nitrile layer is separated and dried over 25 g. of Drierite; it weighs 299–309 g. (90–92%). The crude product is purified by distillation; the portion boiling at 61–63°/14 mm., n_D^{25} 1.4230, amounts to 298–302 g. (88–90%) (Note 1).

2. Note

1. Higher homologs have been prepared from other aldehydes.

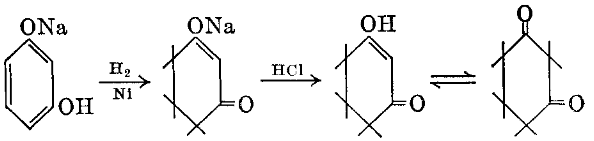
3. Method of Preparation

This procedure is essentially that recorded in the literature.[1]

[1] Knoevenagel and Mercklin, *Ber.*, **37**, 4089 (1904).

DIHYDRORESORCINOL

(1,3-Cyclohexanedione)



Submitted by R. B. THOMPSON.
Checked by NATHAN L. DRAKE, G. FORREST WOODS, and I. W. TUCKER.

1. Procedure

A solution of 24 g. (0.6 mole) of sodium hydroxide, 100 ml. of water, and 55 g. (0.5 mole) of resorcinol is placed in an apparatus for high-pressure hydrogenation together with 10 g. of reduced

Universal Oil Products hydrogenation catalyst (Note 1) or Raney nickel.[1] The pressure in the bomb is raised to 1000–1500 lb. with hydrogen, and the temperature is adjusted to 50° (Note 2). The bomb is shaken and the reaction allowed to proceed for 10 to 12 hours, during which time 0.5 mole of hydrogen is absorbed (Note 3).

The apparatus is allowed to cool to room temperature, the pressure is released, and the catalyst is removed by filtration. The filtrate is made acid to Congo red with concentrated hydrochloric acid, and the solution is cooled to 0° in an ice-salt bath and held at that temperature for 30 minutes before filtration. The dihydroresorcinol which crystallizes is separated by filtration and dried; 50–60 g. of crude dry product containing sodium chloride is obtained.

The crude dihydroresorcinol is dissolved in 125–150 ml. of hot benzene, filtered to remove the sodium chloride, and allowed to crystallize. The solid is separated by filtration and dried overnight in a vacuum desiccator. The product melts at 103–104° and weighs 48–53 g. (85–95%) (Note 4).

2. Notes

1. The Universal Oil Products hydrogenation catalyst consists of a mixture of nickel, nickel oxides, and kieselguhr compressed into pills containing 50–55% nickel. Before use in a liquid-phase hydrogenation of this sort, the catalyst must be reduced in a stream of hydrogen at 430°. The reduced catalyst is cooled in the stream of hydrogen and may be kept under alcohol. It also may be saturated with carbon dioxide and kept in a sealed bottle. The pilled material should be pulverized before use in this preparation. The pelleted Universal Oil Products hydrogenation catalyst may be purchased from Universal Oil Products Company, 310 S. Michigan Ave., Chicago 4, Illinois.

2. It is particularly important that the temperature should not rise above 50°; at higher temperatures complex condensation products result.

3. It is important that hydrogenation be complete; incompletely hydrogenated material yields an oily product which is exceedingly difficult to crystallize. The usual time of hydrogen absorption is 4 to 5 hours with Universal Oil Products catalyst and about 4 hours with Raney nickel. The extra time mentioned in the procedure avoids any chance of incomplete reduction.

4. Dihydroresorcinol is unstable; it can be stored only a short time. If it is not used immediately, it should be stored under an inert gas in a brown bottle in a refrigerator.

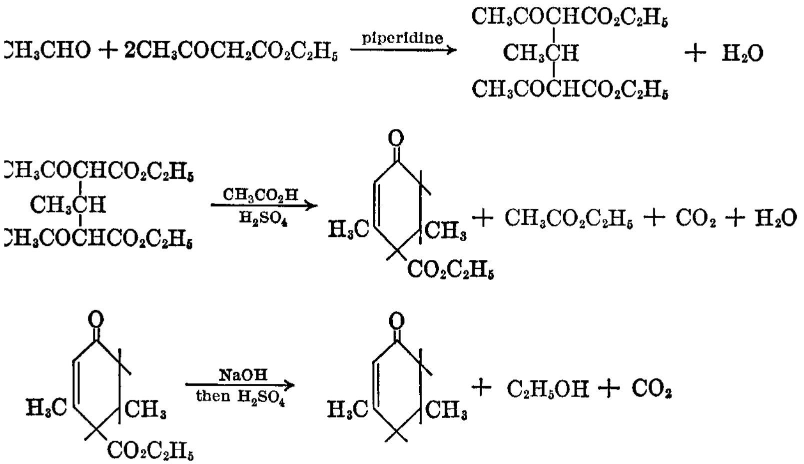
3. Methods of Preparation

Dihydroresorcinol has been prepared by the reduction of resorcinol with sodium amalgam,[2] by reduction of hydroxyhydroquinone or its carboxylic acid with sodium amalgam,[3] by hydrolysis of its dioxime,[4] or by cyclization of ethyl γ-acetylbutyrate.[5] The present method of preparation is essentially that of Klingenfuss.[6]

[1] *Org. Syntheses*, **21**, 15 (1941).
[2] Merling, *Ann.*, **278**, 28 (1894).
[3] Thiele and Jaeger, *Ber.*, **34**, 2841 (1901).
[4] Kötz and Grethe, *J. prakt. Chem.*, (2) **80**, 502 (1909).
[5] Vorländer, *Ann.*, **294**, 270 (1897); Schilling, *Ann.*, **308**, 190 (1899).
[6] Klingenfuss (to Hoffmann-La Roche, Inc.), U. S. pat. 1,965,499 [*C. A.*, **28**, 5476 (1934)].

3,5-DIMETHYL-4-CARBETHOXY-2-CYCLOHEXEN-1-ONE and 3,5-DIMETHYL-2-CYCLOHEXEN-1-ONE

(2-Cyclohexen-1-one, 4-carbethoxy-3,5-dimethyl-, and 2-cyclohexen-1-one, 3,5-dimethyl-)



Submitted by E. C. Horning, M. O. Denekas, and R. E. Field.
Checked by Cliff S. Hamilton and Robert F. Coles.

1. Procedure

A. *3,5-Dimethyl-4-carbethoxy-2-cyclohexen-1-one.* In each of three 500-ml. Erlenmeyer flasks (Note 1) is placed 210 ml. (210 g., 1.61 mole) of ethyl acetoacetate (Note 2). The flasks are placed in an ice-salt bath and chilled to 0°; to each flask there is then added 45 ml. (35.2 g., 0.78 mole) of acetaldehyde. When the contents of the flasks have cooled to −5° to 0° there is added to each flask, with shaking, a solution of 2 ml. of piperidine in 5 ml. of absolute alcohol. The flasks, the contents of which become cloudy in a short time because of the separation of water, are kept in an ice-salt bath for 6 hours. The reaction mixtures are then combined in a 1-l. flask and placed in an icebox.

About 24 hours later, 3 ml. of piperidine in 5 ml. of absolute alcohol is added with shaking, and the flask is replaced in an icebox until the next day. The addition of 3 ml. of piperidine in 5 ml. of absolute alcohol is repeated once more, and the mixture is again returned to the icebox for 24 hours. The mixture is then allowed to stand for at least 1 day at room temperature. At some point during this reaction period the mixture should crystallize as a mass of yellow-white needles (Note 3). This product is crude ethyl ethylidene-*bis*-acetoacetate.

The crude *bis*-ester is melted on a steam cone and poured into a 3-l. round-bottomed flask containing 600 ml. of glacial acetic acid, 40 ml. of concentrated sulfuric acid, and approximately 10 g. of small chips of porous plate (Note 4). The mixture is heated under reflux for 1 hour. There is a copious evolution of carbon dioxide which should be directed to a gas-absorption trap since it is accompanied by acetic acid vapors. The mixture is poured, with mechanical stirring, into 2 l. of ice water in a 4-l. beaker. Enough ether is added to allow separation of the layers (Note 5), and the organic layer is returned to the beaker with 1.2–1.3 l. of water. With the aid of good stirring the mixture is neutralized by slow addition of solid sodium carbonate until the effervescence ceases. The layers are separated, and the material so obtained may be used immediately for the preparation of 3,5-dimethyl-2-cyclohexen-1-one. To obtain 3,5-dimethyl-4-carbethoxy-2-cyclohexen-1-one, the ether solution is washed with 100 ml. of 5% sodium hydroxide solution, then with 100 ml. of water containing 2 ml. of acetic acid, dried over anhydrous magnesium sulfate, and distilled through a short column under reduced pressure. After a very slight fore-run the main fraction is collected at 135–155°/10 mm. This is redistilled through a moderately good column, preferably of the Widmer or Vigreux type. The product is 3,5-dimethyl-4-carbethoxy-2-cyclohexen-1-one, b.p. 136–138°/9 mm. The yield is 220–234 g. (47–50%).

B. *3,5-Dimethyl-2-cyclohexen-1-one.* The ether solution of crude 3,5-dimethyl-4-carbethoxy-2-cyclohexen-1-one obtained as described above is transferred to a 3-l. round-bottomed flask.

The ether is removed on a steam cone, preferably with the aid of an aspirator, and there are added 1140 ml. of water, 60 ml. of alcohol (95%), and 130 g. of sodium hydroxide. The mixture is shaken continuously and heated on a steam cone until the alkali dissolves, and heating is continued on a steam cone with frequent shaking until the ester dissolves (Note 6). The solution is then refluxed for 15 minutes.

The flask is cooled with a stream of water while a solution of 100 ml. of concentrated sulfuric acid in 200 ml. of water is added slowly and cautiously (Note 7). The acidified mixture is heated under reflux for 15 minutes, allowed to cool, and the layers separated. The crude product is diluted with 100 ml. of ether and washed successively with two 100-ml. portions of 5% sodium hydroxide solution and with 100 ml. of water containing 5 ml. of acetic acid. The ethereal solution, after drying over anhydrous magnesium sulfate, is distilled through a short column under reduced pressure. The product boiling at 84–86°/9 mm. is 3,5-dimethyl-2-cyclohexen-1-one; the yield is 155–165 g. (52–55%) (Note 8).

2. Notes

1. The checkers found it more convenient to use a 1-l. Erlenmeyer flask instead of three 500-ml. flasks.

2. The ethyl acetoacetate was obtained from the Carbide and Carbon Chemicals Corporation. The acetaldehyde was obtained from the Niacet Chemicals Corporation. The piperidine was the Practical grade of the Eastman Kodak Company.

3. Crystals may appear before the addition of all the piperidine has been completed. In this event the time of standing as described is followed, but no more catalyst need be added.

4. Ordinary boiling chips are convenient.

5. Usually 150–200 ml. of ether is ample. The layers may be separated in a separatory funnel, or the lower aqueous layer may be removed with a siphon.

6. The solution of the ester is an exothermic process. No attempt should be made to heat the mixture to reflux temperature until the ester has been dissolved.

7. It is important that this step be carried out slowly and with a hot solution. A satisfactory method is to place the flask in a sink while the contents are still hot and to cool with a stream of water directed over the entire flask. The sulfuric acid solution should be poured slowly down the wall of the flask, the rate of addition being regulated by the vigor of the decarboxylation. It is possible to carry out part of the decarboxylation in the alkaline solution by prolonging the reflux period, but this procedure offers no advantage over that described.

8. This general procedure can also be applied to compounds derived from other aliphatic aldehydes.[1]

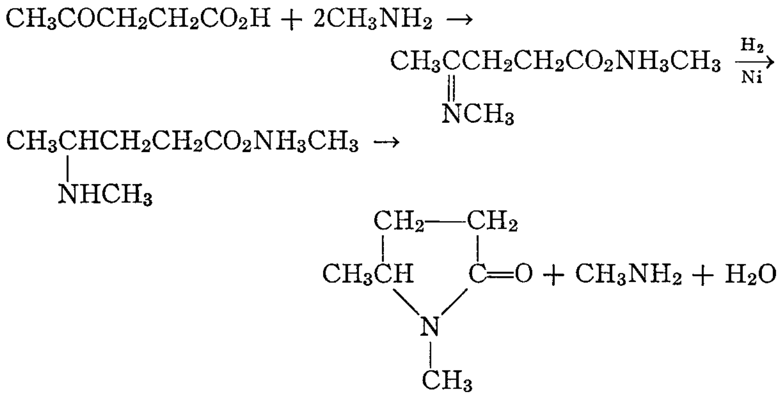
3. Methods of Preparation

3,5-Dimethyl-4-carbethoxy-2-cyclohexen-1-one and 3,5-dimethyl-2-cyclohexen-1-one have always been prepared from acetaldehyde and acetoacetic ester through the Knoevenagel condensation.[2] The keto ester has previously been obtained by selective saponification and decarboxylation methods which have involved heating the crude condensation product with water at 140° [2,3] or with sodium ethoxide in alcohol.[3] The ketone has been obtained from the same condensation product by prolonged refluxing in 20% sulfuric acid.[2,4,5]

[1] Horning, Denekas, and Field, *J. Org. Chem.*, **9**, 548 (1944).
[2] Knoevenagel, *Ann.*, **281**, 104 (1894).
[3] Rabe, *Ann.*, **342**, 344 (1905).
[4] Gatterman, *Practical Methods of Organic Chemistry*, trans. by Schober and Babasinian, p. 202, The Macmillan Company, New York, 1921.
[5] Smith and Roualt, *J. Am. Chem. Soc.*, **65**, 634 (1943).

1,5-DIMETHYL-2-PYRROLIDONE

(2-Pyrrolidone, 1,5-dimethyl-)



Submitted by ROBERT L. FRANK, WILLIAM R. SCHMITZ, and BLOSSOM ZEIDMAN.
Checked by ARTHUR C. COPE and W. H. JONES.

1. Procedure

One hundred and ninety-four grams (170 ml., 1.67 moles) of levulinic acid (Note 1) and 500 ml. of 35% aqueous methylamine (sp. gr., 0.89; 3.94 moles of methylamine) (Note 2) are placed in a 2-l. steel reaction vessel of a high-pressure hydrogenation apparatus.[1] Ten grams of Raney nickel catalyst [2] is added, the vessel is closed, and hydrogen is admitted to a pressure of 1000–2000 lb. The bomb is then heated with continuous agitation to 140° and maintained at that temperature for 5 hours (Note 3). The contents are removed, and the bomb is washed with two 100-ml. portions of water. After removal of the catalyst by filtration (Note 4), the filtrate is distilled under reduced pressure using a modified Widmer column.[3] A low-boiling fore-run of water and methylamine distils first, followed by the product, a colorless liquid boiling at 84–86°/13 mm.; 102–104°/27 mm.; n_D^{25} 1.4611 (Note 5). The yield is 140–146 g. (74–77%).

2. Notes

1. A. E. Staley Manufacturing Company's Grade A levulinic acid was used.
2. Commercial 35% aqueous methylamine solution was used.
3. The course of the reaction may be followed by the drop in hydrogen pressure, the decrease depending upon the size of the bomb employed.
4. Because of its pyrophoric nature, the nickel catalyst should not be allowed to dry on the filter. A convenient alternative procedure for removing catalyst is to centrifuge the reaction mixture.
5. The product of some runs has a light yellow tint, but the color appears to cause no complications in subsequent reactions of the material.

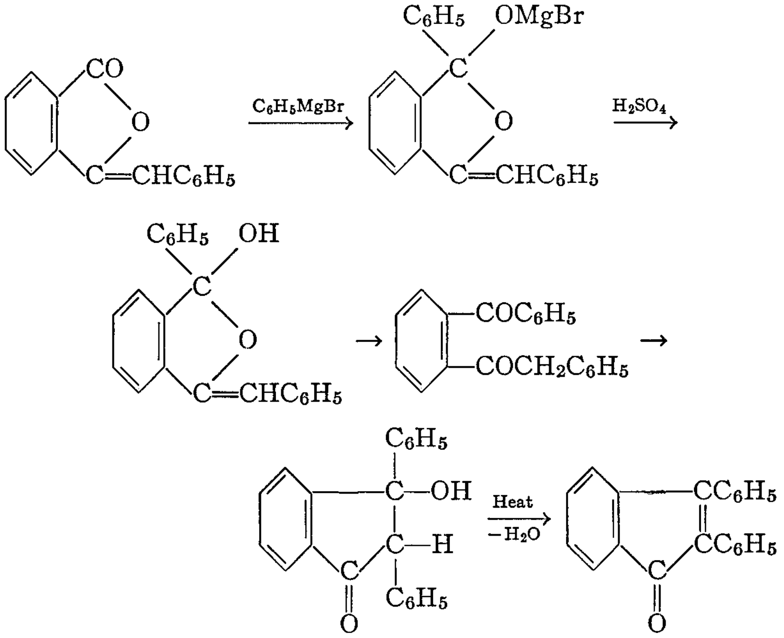
3. Methods of Preparation

1,5-Dimethyl-2-pyrrolidone has been prepared by the reaction of 5-methyl-2-pyrrolidone with excess methyl iodide[4] and by the catalytic hydrogenation of a mixture of levulinic acid and methylamine.[5]

[1] Suitable equipment may be obtained from the American Instrument Company, Silver Spring, Maryland, and the Parr Instrument Company, Moline, Illinois.
[2] *Org. Syntheses*, **21**, 15 (1941).
[3] Smith and Adkins, *J. Am. Chem. Soc.*, **60**, 663 (1938).
[4] Senfter and Tagel, *Ber.*, **27**, 2313 (1894).
[5] Hoffman-La Roche and Company, Ger. pat. 609,244 [*C. A.*, **29**, 3116 (1935)].

2,3-DIPHENYLINDONE (2,3-DIPHENYL-1-INDENONE)

(Indone, 2,3-diphenyl-)



Submitted by C. F. H. ALLEN, J. W. GATES, JR., and J. A. VANALLAN.
Checked by R. L. SHRINER and H. W. JOHNSTON.

1. Procedure

A solution of phenylmagnesium bromide is prepared in the usual manner[1] using 12.2 g. (0.5 gram atom) of magnesium, 78.5 g. (52 ml., 0.5 mole) of bromobenzene, and 500 ml. of absolute ether in a 2-l. round-bottomed, three-necked flask fitted with a reflux condenser, a mechanical stirrer, and a dropping funnel. No unreacted magnesium should remain; if any does, an additional 1 to 2 ml. of bromobenzene should be added.

To this vigorously stirred solution is added slowly a solution of 44.5 g. (0.20 mole) of benzalphthalide[2] in 400 ml. of dry benzene. After about half of this solution has been added, the magnesium complex begins to separate; it hinders the stirring somewhat. When all the phthalide solution has been admitted (about 1 hour), the reflux condenser is replaced by a still head carrying a thermometer and attached to a condenser set for downward distillation. The bulk of the solvent is then removed; this requires about 30 minutes, the temperature of the vapor remaining at 50° for about half this time and rising to about 65° toward the end. About 220–230 ml. of distillate is obtained. The flask and contents are then immersed in an ice bath, and the magnesium complex is decomposed by the slow addition of a cold solution of 15 ml. of concentrated sulfuric acid in 300 ml. of water (Note 1) with rapid stirring. The upper benzene layer is separated and transferred to a 1-l. Claisen flask, and the solvent is removed by distillation from a steam bath; this requires about 4 hours. The residual thick red syrup is transferred to a 125-ml. Claisen flask with a wide side arm set up for vacuum distillation. The residue is heated under a pressure of about 10 mm. to remove all low-boiling material (Note 2) and then distilled under reduced pressure. The fraction boiling at 215–255°/6 mm. (195–220°/1 mm.) is collected, most of the distillate coming over at 235–240°/6 mm. The distillate is dissolved in 50 ml. of boiling benzene, 200 ml. of hot 95% ethanol is added, and the solution is chilled in an ice bath for 2 hours. The red, crystalline 2,3-diphenylindone is collected on a filter, washed with 50 ml. of cold 95% ethanol, and air dried. The yield is 34–40 g. (60–71%) of red crystals melting at 149–151° (Notes 3 and 4).

2. Notes

1. The decomposition is vigorous, and the acid must be admitted slowly at first but may be added more rapidly toward the end.

2. During this heating any carbinol present is dehydrated. Low and erratic yields usually indicate incomplete dehydration.

3. The product may be recrystallized by dissolving it in 50 ml. of boiling benzene and diluting with 200 ml. of hot ethanol. The recovery of material, m.p. 150–151°, is about 90%.

4. This procedure is capable of considerable variation, by which other indenones may be secured. For example, the benzalphthalide may be replaced by other phthalides made from (*a*) other aldehydes, or (*b*) other anhydrides; the phenylmagnesium bromide can be replaced by other Grignard reagents.

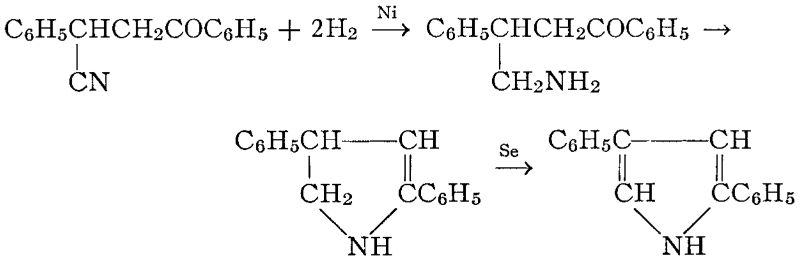
3. Methods of Preparation

2,3-Diphenylindone has been prepared by the action of phenylmagnesium bromide upon benzalphthalide [3,4] and by ring closure from α,β-diphenylcinnamic acid.[5,6]

[1] *Org. Syntheses* Coll. Vol. **1**, 226 (1941).
[2] *Org. Syntheses* Coll. Vol. **2**, 61 (1943).
[3] Löwenbein and Ulich, *Ber.*, **58**, 2662 (1925).
[4] Weiss and Sauermann, *Ber.*, **58**, 2736 (1925).
[5] Meyer and Weil, *Ber.*, **30**, 1281 (1897).
[6] Weitz and Scheffer, *Ber.*, **54**, 2341 (1921).

2,4-DIPHENYLPYRROLE

(Pyrrole, 2,4-diphenyl-)



Submitted by C. F. H. Allen and C. V. Wilson.
Checked by Arthur C. Cope, Frank S. Fawcett, and Harold R. Nace.

1. Procedure

A suspension of 61 g. (0.26 mole) of α-phenyl-β-benzoylpropionitrile [1] (Note 1) in 150 ml. of methyl alcohol and 1 level teaspoonful of Raney nickel catalyst [2,3] (Note 2) are placed in a 400–500 ml. pressure bottle (Note 3) connected to a low-pressure reduction apparatus.[4] The bottle is alternately evacuated and filled with hydrogen twice, and the reduction is conducted at 80–90° by shaking with hydrogen at an initial pressure of 50 lb. After 2 moles of hydrogen are absorbed the reduction is discontinued, the solution is filtered to separate the catalyst, and the solvent is removed from the green filtrate by distillation under reduced pressure. The crude 2,4-diphenyl-2-pyrroline (Note 4) is rinsed into a 300-ml. Kjeldahl flask with a little methyl alcohol, which is removed by distillation at reduced pressure (water pump) while the flask is immersed in a bath at 100°. Selenium (10 g.) is added, and the mixture is heated in a metal bath at 245–265° for 5 hours while a slow stream of nitrogen is passed over the surface of the liquid. This operation is conducted in a well-ventilated hood. The molten mass is

poured from the reaction flask into a beaker (Note 5), and the product is extracted with 300 ml. of boiling toluene. The green toluene solution is filtered through a cotton plug to remove a small amount of suspended selenium, and the filtrate is cooled. The 2,4-diphenylpyrrole separates as light green crystals which melt at 174–176° and weigh 24–26 g. (42–46%) (Note 6). A second crop of 2–3 g. (4–5%), m. p.160–170°, can be obtained by concentrating the filtrate and cooling.

2. Notes

1. The α-phenyl-β-benzoylpropionitrile[1] was used without recrystallization (m.p. 123–125°).

2. The time required for the hydrogenation was 2.5 hours with a very active nickel catalyst, and longer with a less active catalyst. Raney nickel prepared according to Reference 2 is a particularly active catalyst and gives excellent results in this preparation.

3. A 500-ml. Pyrex centrifuge bottle is satisfactory.

4. The submitters state that distillation yields pure 2,4-diphenyl-2-pyrroline, b.p. 170–172°/3 mm., 203–205°/8 mm., which solidifies on cooling (yield 80–90%).

5. If the contents of the flask are not poured into a beaker while molten, it is difficult to remove the cake of selenium. If more than one preparation is to be made, the contents of the flask are allowed to cool and the product is extracted with hot toluene. The selenium can be reused.

6. The product is sufficiently pure for most purposes. Recrystallization from toluene gives a 90–93% recovery of a very light green product, m.p. 179–180° (cor.). The submitters state that the product obtained in the first crystallization has this melting point if the 2,4-diphenyl-2-pyrroline is purified by distillation before dehydrogenation.

3. Methods of Preparation

2,4-Diphenylpyrrole has been prepared only by dehydrogenation of 2,4-diphenyl-2-pyrroline with selenium, Raney nickel, and nickel supported on pumice.[5]

[1] *Org. Syntheses* Coll. Vol. **2**, 498 (1943).
[2] Pavlic and Adkins, *J. Am. Chem. Soc.*, **68**, 1471 (1946).
[3] *Org. Syntheses*, **21**, 15 (1941).
[4] *Org. Syntheses* Coll. Vol. **1**, 61 (1941).
[5] Rogers, *J. Chem. Soc.*, **1943**, 594.

ETHYL α-ISOPROPYLACETOACETATE

(Isovaleric acid, α-acetyl, ethyl ester)

$$CH_3COCH_2CO_2C_2H_5 + (CH_3)_2CHOH \xrightarrow{BF_3} CH_3COCH((CH_3)_2CH)CO_2C_2H_5 + H_2O$$

Submitted by JOE T. ADAMS, ROBERT LEVINE, and CHARLES R. HAUSER.
Checked by H. R. SNYDER and JOHN MIRZA.

1. Procedure

This reaction should be carried out under a well-ventilated hood (Note 1).

A mixture of 30.0 g. (0.5 mole) of anhydrous isopropyl alcohol and 65.0 g. (0.5 mole) of freshly distilled ethyl acetoacetate is placed in a 500-ml. round-bottomed three-necked flask equipped with a mercury-sealed stirrer, a gas inlet tube terminating about 1 cm. above the surface of the liquid, a gas outlet tube connected with a calcium chloride drying tube, and a thermometer (Note 2). The gas inlet tube is connected to a source of boron fluoride (Note 3), and an ice bath is applied to the reaction flask; when the temperature of the stirred mixture has fallen to approximately 0° the stream of boron fluoride is started and adjusted so that the temperature of the mixture does not exceed 7°. The addition of

boron fluoride is continued until the mixture is saturated and for 15 minutes thereafter (Note 4). The reaction mixture then is stirred at 28° for 2.5 hours (Note 5), at the end of which period it is poured slowly into a stirred mixture of 130 g. of hydrated sodium acetate, 100 ml. of water, and 200 g. of crushed ice. The beaker containing the resulting mixture is allowed to stand in an ice bath for 2 hours with occasional stirring.

The mixture is poured into a 1-l. separatory funnel. The beaker is rinsed with 300 ml. of ether, and this portion of solvent is shaken with the mixture in the separatory funnel. The phases are separated, and the aqueous solution is extracted twice with 100-ml. portions of ether. The combined ether solutions are washed with saturated aqueous bicarbonate solution until carbon dioxide no longer forms. The solution is transferred to an Erlenmeyer flask and dried over about 25 g. of anhydrous sodium sulfate for 12 hours, after which it is decanted into another Erlenmeyer flask and dried over about 10 g. of Drierite for 6 hours.

A 125-ml. modified Claisen flask is arranged for distillation, but with a dropping funnel fitted in the neck intended for the ebullator tube. Portions of the dried ether solution are introduced into the flask through the funnel while the flask is heated on the steam bath for continuous removal of the solvent. After all the ether solution and the ether washings from the last drying agent have been concentrated, the dropping funnel is replaced by an ebullator tube and distillation under diminished pressure is begun cautiously. Fractions are collected at 60–96°/20 mm. and at 96–98°/20 mm. The first fraction is redistilled to give an additional quantity of material boiling at 96–98°/20 mm. (Note 6). The combined product weighs 52–58 g. (60–67%) (Note 7).

2. Notes

1. Although no definite data are available concerning the toxicity of boron flouride, users should exercise caution and avoid breathing the fumes. The toxic effects of hydrogen fluoride and alkali fluorides are well known. Boron fluoride reacts with moisture in the air, forming white fumes of fluoboric acid and boric acid which cause a choking sensation when breathed.

2. The entire apparatus is dried in an oven at about 100° just before use.

3. Commercial boron fluoride from a tank is passed through a saturated solution of boric oxide in concentrated sulfuric acid.

4. The time required for saturation varies from 1 to 2 hours, depending upon the rate of addition. As the saturation point is approached, the fuming at the end of the exit tube increases rather sharply; the mixture is considered to be saturated when the fuming appears to have become constant.

5. The temperature and time at this point are critical and must be controlled carefully.

6. If the fractionation is conducted with a 30-cm. Vigreux column the redistillation of the fore-run is unnecessary.

7. By the same method ethyl α-cyclohexylacetoacetate (b.p. 146–148°/20 mm.) has been prepared in 34% yield from cyclohexanol and acetoacetic ester, and ethyl α-*tert.*-butylacetoacetate (b.p. 101–102°/20 mm.) in 10–14% yield from *tert.*-butyl alcohol and acetoacetic ester.

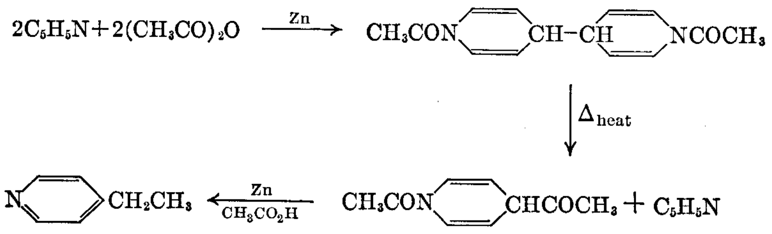
3. Methods of Preparation

The above procedure is based on that described by Adams, Abramovitch, and Hauser.[1] Ethyl α-isopropylacetoacetate has also been prepared by Hauser and Breslow [2] by the reaction of ethyl acetoacetate with isopropyl ether in the presence of boron trifluoride and by Bischoff [3] by the alkylation of the sodium derivative of ethyl acetoacetate with isopropyl iodide.

[1] Adams, Abramovitch, and Hauser, *J. Am. Chem. Soc.*, **65**, 552 (1943).
[2] Hauser and Breslow, *J. Am. Chem. Soc.*, **62**, 2389 (1940).
[3] Bischoff, *Ber.*, **28**, 2620 (1895).

4-ETHYLPYRIDINE

(Pyridine, 4-ethyl-)



Submitted by ROBERT L. FRANK and PAUL V. SMITH.[1]
Checked by HOMER ADKINS and ROBERT H. JONES.

1. Procedure

In a 3-l. three-necked, round-bottomed flask fitted with a Hershberg stirrer and a thermometer are placed 1500 ml. of acetic anhydride and 300 g. (306 ml., 3.80 moles) of dry pyridine (Note 1). Three hundred grams (4.6 gram atoms) of zinc dust (Note 2), in amounts of 5–10 g., is added with stirring over a period of 3 hours. Heat is evolved almost immediately, and a cooling bath of water may be necessary. The reaction mixture becomes green after about 20 minutes. The temperature of the contents of the flask should be maintained between 25° and 30°. After the addition of the first 300-g. portion of zinc, 300 ml. of acetic acid is added to the reaction mixture and a reflux condenser is attached to the flask. Then 120 g. (1.83 gram atoms) of zinc dust is added in small portions. Heat is evolved during the addition, and the reaction may become rather violent. The mixture is refluxed with stirring for 30 minutes. A third portion of 180 g. (2.75 gram atoms) of zinc dust is added all at once, and refluxing is continued for an additional half hour. The solution is now orange-brown.

The flask is allowed to cool, and the contents are transferred to a 5-l. round-bottomed flask. The mixture is cautiously

neutralized with 2 l. of a 40% aqueous solution of sodium hydroxide. The mixture is steam-distilled until 3 l. of distillate is collected, after which the residue is discarded. The distillate, which separates into two layers, is saturated with 1500–1800 g. of solid potassium carbonate (Note 3). The organic layer is removed by decantation; the remaining water layer is divided into two portions, and each is extracted once with 150 ml. of chloroform. The chloroform extracts are combined with the organic layer.

The mixture is distilled using an efficient fractionating column (Note 4). There is a large fore-run of chloroform, pyridine, and water (Note 5), after which the temperature rises and 145–167 g. of material, b.p. 145–165°/760 mm., is collected. This is refractionated, and 135–155 g. (33–38%) of 4-ethylpyridine, b.p. 163–165°/760 mm.; n_D^{20} 1.5010, is obtained (Note 6).

2. Notes

1. The pyridine is dried over calcium oxide and redistilled.

2. The zinc is activated before use by stirring 830 g. of zinc dust in 300 ml. of 10% hydrochloric acid for 2 minutes, filtering, and washing the zinc with 600 ml. of water, then with 200 ml. of acetone.

3. An equal weight of sodium chloride may be used instead of potassium carbonate.

4. A Fenske-type column 30 cm. in length and 18 mm. in diameter packed with glass helices gave satisfactory separations.

5. It does not appear feasible to recover the pyridine from the mixture of chloroform, water, and pyridine.

6. This procedure has been employed by Arens and Wibaut[2] to prepare other 4-alkyl derivatives of pyridine. The yields tend to decrease as the molecular weight of the anhydride increases. The boiling points are as given below: 4-propylpyridine 189°, 4-*n*-butylpyridine 207–209°, 4-isobutylpyridine 197–199°, 4-isoamylpyridine 222–223°, and 4-*n*-octylpyridine 265–268°.

3. Methods of Preparation

4-Ethylpyridine has been prepared by heating N-ethylpyridinium iodide in a sealed tube at 300°;[3] by heating pyridine with ethyl iodide;[4] from 4-ethylpyridinecarboxylic acid through distillation from lime;[5] and in small amounts by distilling brucine with potassium hydroxide.[6] Pyridine when heated with ferric chloride in an autoclave gives a mixture of alkylated pyridines from which 4-ethylpyridine can be isolated.[7] A general method for 4-alkylpyridines involves heating 5-(γ-pyridyl)-5-alkylbarbituric acids with alkali followed by an acid cleavage to remove the carbon dioxide.[8] 4-Ethylpyridine has been isolated from California petroleum.[9] The most useful method involves the treatment of pyridine with acetic anhydride and zinc.[10,11]

[1] Work done under contract with the Office of Rubber Reserve, Reconstruction Finance Corporation.
[2] Arens and Wibaut, *Rec. trav. chim.*, **61**, 59 (1942).
[3] Ladenburg, *Ber.*, **16**, 2059 (1883); **18**, 2961 (1885); *Ann.*, **247**, 1 (1888).
[4] Ladenburg, *Ber.*, **32**, 42 (1899).
[5] Gabriel and Colman, *Ber.*, **35**, 1358 (1902).
[6] Oechsner de Coninck, *Ann. chim.*, (5) **27**, 507 (1882).
[7] Morgan and Burstall, *J. Chem. Soc.*, **1932**, 20.
[8] Gebauer (Chemische Fabrik von Heyden, A.-G.), Ger. pat. 638,596 [*C. A.*, **31**, 3067 (1937)].
[9] Hackmann, Wibaut, and Gitsels, *Rec. trav. chim.*, **62**, 229 (1943).
[10] Dohrn and Horsters (Chemische Fabrik auf Actien vorm. E. Schering), Ger. pat. 390,333 [*Chem. Zentr.*, **1924**, II, 891].
[11] Wibaut and Arens, *Rec. trav. chim.*, **60**, 119 (1941).

GLYCOLONITRILE

$$CH_2O + KCN + H_2O \rightarrow HOCH_2CN + KOH$$

Submitted by Roger Gaudry.
Checked by C. F. H. Allen and J. A. VanAllan.

1. Procedure

This preparation should be carried out under a good hood since poisonous hydrogen cyanide may be evolved.

In a 1-l. three-necked flask, fitted with a stirrer, thermometer for reading low temperatures, and a dropping funnel, and surrounded by an ice-salt bath, is placed a solution of 130 g. (2.0 moles) of potassium cyanide in 250 ml. of water. With stirring, a solution of 170 ml. (2.0 moles) of commercial 37% formaldehyde solution [1] and 130 ml. of water is admitted slowly from the dropping funnel at such a rate that the temperature never rises above 10° (about 40 minutes is required). After 10 minutes' standing, 230 ml. of dilute sulfuric acid (57 ml. of concentrated sulfuric acid, sp. gr. 1.84, in 173 ml. of water) is added with stirring, the same low temperature being maintained. A copious precipitate of potassium sulfate is formed. The *p*H of the solution is then about 1.9. A 5% potassium hydroxide solution is then added, dropwise, and with cooling, until the *p*H is about 3.0 (determined either by means of a *p*H meter or tropaeolin 00 paper); about 4 ml. of the solution is required. The flask is then removed from the cooling bath, 30 ml. of ether is added, and the mixture is well shaken. The salt is removed by filtration, using a 14-cm. Büchner funnel, and washed with 30 ml. of ether. The filtrate is poured into a 1-l. continuous ether extractor [2] and extracted for 48 hours with 300 ml. of ether (Note 1). The ether extract is dried for 3–4 hours over 15 g. of anhydrous calcium sulfate (Drierite) (Note 2) and filtered. Ten milliliters of absolute ethanol is added to the filtrate, and the ether is removed on a steam bath (Note 3). The residue is distilled under reduced

pressure using a flask having a Vigreux side arm. After a small (2–3 ml.) fore-run, the glycolonitrile distils smoothly at 86–88°/8 mm. (102–104°/16 mm.). The yield of pure glycolonitrile (Note 4) amounts to 86.5–91 g. (76–80%).

2. Notes

1. It is impractical to extract more than 40–45% of the nitrile without using a continuous ether extractor. A slightly lower yield is obtained if the extraction is continued for only 24 hours. The reaction mixture may be extracted in portions if the available flask is smaller than that specified.

2. Anhydrous sodium sulfate can be used equally well, but its drying action is slower, at least 24 hours being advisable.

3. If the alcohol is omitted, the nitrile shows a strong tendency to polymerize during the removal of the ether, especially when most of the ether has distilled.

4. The alcohol serves as a preservative before and after the distillation. Glycolonitrile obtained without the use of alcohol usually cannot be kept more than a few days; it sometimes turns brown within 24 hours. Some samples of alcohol-stabilized glycolonitrile have been preserved in sealed bottles for two years, whereas other samples polymerized in a few months.

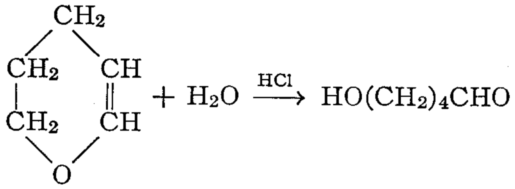
3. Methods of Preparation

Glycolonitrile has usually been prepared by the interaction of formaldehyde and an alkali cyanide in aqueous solution [3] of which the procedure outlined is a modification. A recent development is the cyanohydrin interchange method.[4, 5]

[1] *Org. Syntheses* Coll. Vol. **1**, 378, Note 1 (1941).
[2] *Org. Syntheses* Coll. Vol. **2**, 378 (1943).
[3] Polstorff and Meyer, *Ber.*, **45**, 1911 (1912).
[4] Kung, U. S. pat. 2,259,167 [*C. A.*, **36**, 494 (1942)].
[5] Mowry, *J. Am. Chem. Soc.*, **66**, 372 (1944).

5-HYDROXYPENTANAL

(Valeraldehyde, δ-hydroxy-)



Submitted by G. FORREST WOODS, JR.
Checked by CLIFF S. HAMILTON and WM. V. RUYLE.

1. Procedure

In a 1-l. three-necked flask provided with a Hershberg stirrer are mixed 300 ml. of water, 25 ml. of concentrated hydrochloric acid (Note 1), and 100 g. of 2,3-dihydropyran.[1] The mixture is stirred until the solution has become homogeneous and then for an additional 20 minutes (Note 2). After the addition of a few drops of phenolphthalein indicator to the mixture, the acid is neutralized with 20% sodium hydroxide; enough alkali is added so that a faint pink color just persists.

The solution is then transferred to a continuous extractor and extracted with ether for about 16 hours. The ether extract is added in convenient portions to a 250-ml. modified Claisen flask fitted with a condenser and a suitable fraction-cutter for distillation under reduced pressure. The ether is removed by distillation under the diminished pressure of a water pump, and the residue is then distilled at about 10 mm. pressure. After a small fore-run which weighs 2–5 g., the product distils as a clear, colorless, viscous oil at 62–66°/9–10 mm.; n_D^{25} 1.4513. The yield is 90–95 g. (74–79%) (Notes 3 and 4).

2. Notes

1. The quantity of acid is arbitrary. This amount was chosen to minimize the time of hydration. The order of addition of the reactants should be that stated above. Less acid may be used with increased reaction time; more should not be used.

2. About 5–10 minutes is required before the solution becomes homogeneous. Some heat is evolved during the hydration. The submitter has found that the amount of 2,3-dihydropyran may be increased up to 300 g. without using more water or acid; however, if larger quantities of the pyran are used, the pyran must be added dropwise to the acid solution with cooling.

3. A convenient apparatus for the distillation is a modified Claisen flask whose side arm is provided with a short water-cooled condenser. A fraction-cutter of the "pig" type is satisfactory.

4. According to the submitter the product can be converted smoothly to pentamethylene glycol by hydrogenation over Raney nickel at 90° and 2000 lb. pressure. It will also undergo reductive alkylamination by a procedure similar to that described for 2-isopropylaminoethanol.[2]

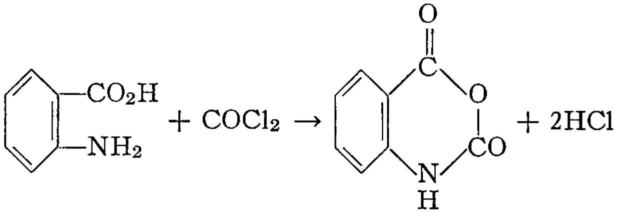
3. Methods of Preparation

5-Hydroxypentanal has been prepared only by the method of Paul,[3] of which the above is an adaptation.

[1] *Org. Syntheses*, **23**, 25 (1943).
[2] *Org. Syntheses*, **26**, 38 (1946).
[3] Paul, *Bull. soc. chim.*, (5), **1**, 976 (1934).

ISATOIC ANHYDRIDE

(N-Carboxyanthranilic anhydride)



Submitted by E. C. Wagner and Marion F. Fegley.
Checked by R. L. Shriner and R. M. Hedrick.

1. Procedure

Phosgene is toxic. The apparatus should be set up in a good hood.

One hundred and thirty-seven grams (1 mole) of anthranilic acid is dissolved, with the aid of gentle warming, in a mixture of 1 l. of water and 126 ml. of concentrated hydrochloric acid (sp. gr. 1.19). The solution is filtered into a 2-l. three-necked flask fitted with a gas-tight, mechanically driven Hershberg stirrer.[1] Through one of the side necks extends an inlet tube which ends in a coarse sintered glass gas-dispersing tip extending well into the liquid in the flask. The inlet tube is connected with a cylinder of phosgene through an empty safety flask. In the third neck of the flask is mounted an addition tube, through the vertical arm of which a thermometer (Note 1) is mounted so that the bulb is immersed in the reaction liquid. The outlet tube is attached to the lateral arm of the addition tube and is connected to an empty safety flask which in turn is connected to a Drechsel bottle charged with ammonium hydroxide.

With the stirrer in rapid motion (Note 2) phosgene is passed into the solution of anthranilic acid at such a rate that bubbles of gas escape slowly into the ammonia scrubber (about two

bubbles per second). Isatoic anhydride appears as a precipitate soon after the stream of phosgene is started. The temperature rises but is prevented from exceeding 50° (Note 3) by regulation of the rate at which phosgene is introduced. The stream of phosgene is continued for 2 to 4 hours, or until the rate of absorption is clearly much decreased (Note 4). The flask is disconnected, and residual phosgene is blown out by passing a current of air through the mixture. The product is collected on a Büchner funnel and is washed with three 500-ml. portions of cold water. The first crop amounts to 54–56 g.

The mother liquor is returned to the reaction flask, the apparatus reassembled, and the passage of phosgene resumed (Note 5). When the rate of absorption has noticeably decreased (60 to 90 minutes) the precipitated isatoic anhydride is collected on a filter and washed. The second crop amounts to 34–54 g. A third passage of phosgene at a considerably reduced rate will often yield a small additional crop (10 to 24 g.) of isatoic anhydride (Note 6).

The product is dried in air and then at 100°. The total yield is 118–123 g. (72–75%) of a white or nearly white product which decomposes at 237–240° cor.; this material is pure enough for most purposes. It may be recrystallized from 95% ethanol (about 30 ml. per gram) or from dioxane (about 10 ml. per gram). The former solvent permits the higher recovery (89–90%) and, except for the large volume required, is to be preferred. The mother liquor may be used for recrystallization of several successive lots of isatoic anhydride. The purified compound decomposes at 243° cor. (Note 7).

2. Notes

1. A thermometer with the graduation marks on the upper half of the stem is convenient.

2. The rate of absorption of phosgene is dependent upon the speed and efficiency of the stirring. This also determines the amount of product obtained in each treatment with phosgene.

3. Operation below room temperature is without advantage. At 60° or above the yield of isatoic anhydride is decreased, or the process may yield precipitated material from which little or no isatoic anhydride can be obtained. Cooling of the mixture might become advisable during operation on a scale larger than specified.

4. It is advisable to precipitate the isatoic anhydride in several successive crops as directed, rather than to attempt to complete the reaction in one step, because the accumulation of precipitated isatoic anhydride slows the rate of absorption of phosgene to such an extent that prolonged passage of the gas at a decreasing and eventually very low rate would be necessary.

5. It is important to clean the glass gas-dispersing tip with hot dioxane before reassembling the apparatus.

6. A small (usually trifling) final crop of isatoic anhydride can be obtained by addition of 40 g. (1 mole) of sodium hydroxide to the liquid and by introducing phosgene slowly.

7. The method is capable of extension to other *o*-aminocarboxylic acids,[3] e.g., to 3-amino-2-naphthoic acid, 4,4′-diaminobiphenyl-3,3′-dicarboxylic acid, and 2-amino-*p*-toluic acid. With some acids other than anthranilic, difficulty may be encountered owing to the readiness with which their hydrochlorides are salted out of solution by hydrochloric acid.

3. Methods of Preparation

Isatoic anhydride has been prepared by prolonged refluxing of a mixture of anthranilic acid and ethyl chlorocarbonate,[2] a reaction usually accompanied by formation of considerable monoethyl or/and diethyl isatoate; or by action of phosgene upon anthranilic acid in a solution the acidity of which is moderated by occasional addition of sodium carbonate.[2] The method described is based upon a patented procedure[3] in which, under conditions not fully specified, phosgene is passed into a solution of anthranilic acid hydrochloride with no subsequent adjustment of the acidity.

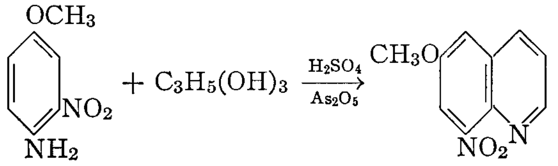
[1] *Org. Syntheses* Coll. Vol. **2**, 117 (1943).

[2] Erdmann, *Ber.*, **32**, 2159 (1899).

[3] Ger. pat. 500,916 [*Frdl.*, **17**, 500 (1930)]; Clark and Wagner, *J. Org. Chem.*, **9**, 60 (1944).

6-METHOXY-8-NITROQUINOLINE

(Quinoline, 6-methoxy-8-nitro-)



Submitted by Harry S. Mosher, William H. Yanko, and Frank C. Whitmore.
Checked by R. L. Shriner, C. E. Kaslow, and Mason Hayek.

1. Procedure

This preparation must be carried out with careful attention to the times and temperatures specified, since Skraup reactions are likely to become violent. The operator should wear goggles, and there should be a safety shower close at hand.

In a 5-l. three-necked, round-bottomed flask, a homogeneous slurry of the following compounds is made by mixing in the order given (Note 1): 588 g. (2.45 moles) of powdered arsenic oxide (Note 2), 588 g. (3.5 moles) of 3-nitro-4-aminoanisole (Note 3), and 1200 g. (950 ml., 13 moles) of U.S.P. glycerol. The flask is fitted with an efficient mechanical stirrer and a 500-ml. dropping funnel in which is placed 315 ml. (579 g., 5.9 moles) of concentrated sulfuric acid (sp. gr. 1.84). With good mechanical stirring the sulfuric acid is dropped into the orange reaction mixture over a period of 30–45 minutes. During this addition, the temperature spontaneously rises to 65–70°.

The stirrer and dropping funnel are removed, and a thermometer is inserted in one neck of the flask by means of a stopper so that the bulb is well below the surface of the reaction mixture. A 10-mm. bent glass tube is attached to the second neck by a rubber stopper and attached through a trap to a water aspirator (Note 4). The third neck is closed with a stopper, and the flask and its contents are weighed. The flask, clamped in place in an oil bath which rests on a hot plate (Note 5), is evacuated, and heat is carefully applied at such a rate that the internal temperature slowly rises to 105° (Note 6). The mixture is kept between 105° and 110° until the loss in weight amounts to 235–285 g. (Note 7), which requires approximately 2–3 hours, depending on the efficiency of the aspirator. If the temperature shows any tendency to rise above 110°, the oil bath should be lowered and the mixture cooled.

When the removal of the water is complete, the suction tube is removed and the stirrer and dropping funnel are replaced. The internal temperature is raised with extreme care to 118° and is held rigidly between 117° and 119° during the subsequent addition of 438 g. (236 ml.) of concentrated sulfuric acid (sp. gr. 1.84) from the dropping funnel. The sulfuric acid must be added dropwise over a period of 2.5–3.5 hours, and the temperature *must not* vary from 117–119° (Note 8). After the addition is complete the temperature is maintained at 120° for 4 hours (Note 9) and finally at 123° for 3 hours. The reaction mixture is cooled below 100°, diluted with 1.5 l. of water, and allowed to cool overnight, preferably with stirring (Note 10). The diluted reaction mixture is poured with stirring into a mixture of 1.8 l. (1580 g.) of concentrated ammonium hydroxide (sp. gr. 0.9) and 3.5 kg. of ice in a 12-l. enameled pail. The resultant thick slurry is filtered through a large Büchner funnel (24–30 cm.), and the filtrate is discarded. The earth-colored precipitate is washed with four 700-ml. portions of water and then transferred to a 3-l. beaker and stirred with 1 l. of methanol for 15 minutes. The slurry is filtered and this process repeated (Note 11). The crude product at this point is a light chocolate brown and weighs about 800 g. when dried. It is purified by boiling for 30 minutes with 4.5 l. of chloroform (Note 12) to which has been added 30 g. of decolorizing carbon. The carbon and other humus-like material are removed by filtration from the hot chloroform solution by means of a 24-cm. warm Büchner funnel. The insoluble material is boiled with 500 ml. of chloroform, the resultant mixture filtered, and the combined filtrates concentrated by distil-

lation from a steam bath to a volume of 1.5–2.5 l., at which point crystals of the 6-methoxy-8-nitroquinoline separate. The solution is then cooled to 5° and the first crop of crystals obtained by collection on a 24-cm. Büchner funnel. The crystals are transferred to a 1-l. beaker, stirred with 400 ml. of methanol for 15 minutes, and again collected on a Büchner funnel and washed with 200 ml. of methanol. The product consists of light tan crystals which weigh 435–500 g. and melt at 158–160° (Note 13). By concentrating the filtrate to 400–500 ml., a second crop of crystals weighing 25–65 g. is obtained which, after washing with methanol in the same way as above, melts at 158–159°. The total yield is 460–540 g. (65–76%) (Notes 14, 15).

2. Notes

1. It is desirable to carry out the reaction without interruption. In order to do this, it is best to set up the apparatus and mix the arsenic oxide, 3-nitro-4-aminoanisole, and glycerol on one day and start the sulfuric acid addition the first thing in the morning of the following day. If the reaction must be interrupted, it can be allowed to cool after it has been heated under reduced pressure. The yield is not affected, but great care must be exercised in reheating the reaction mixture since it sets to a glass, and it is very easy to superheat the outer portions while the center is still cold. If this happens, vigorous decomposition is very likely to occur.

2. Although powdered arsenic oxide was used, probably an equivalent amount of any form of the oxide, such as syrupy arsenic acid, would be suitable since the excess water would be removed when heated under reduced pressure.

3. The 3-nitro-4-aminoanisole was the technical commercial product, m.p. 124–126°, obtained from E. I. du Pont de Nemours and Company.

4. It is desirable to have a manometer in the system. The pressure should drop to approximately 30 mm. as the temperature approaches 105°. If, during the initial evacuation, foaming occurs, it will be necessary to loosen the stopper on the reaction flask or trap and let in air until foaming subsides and steady bubbling commences.

5. The oil bath can be heated by a hot plate which is connected in series to a variable resistance for temperature control. It may be heated with a Bunsen burner, but the temperature of the reaction must then be watched continually. The flask should be clamped in place in such a manner that the source of heat can be removed quickly if necessary.

6. The external temperature may be kept at about 110–115° but should not be raised above this, particularly after the internal temperature has reached 105°. If the temperature rises uncontrolled at this point, complete decomposition of the reaction mixture will result.

7. The loss in weight is dependent upon the quality of the arsenic oxide and glycerol used. If these are dry, the weight loss should be as indicated. The lower figure is equivalent to 1 mole of water for each mole of glycerol.

8. The success of the reaction depends upon the temperature control at this and subsequent points. Since the temperature is dependent upon at least four variables—the rate of addition of sulfuric acid, the rate of stirring, the heat of reaction which decreases as the reaction proceeds, and the heat applied—the temperature must be watched very closely. Too rapid addition of the sulfuric acid during the initial stages of the addition will result in an uncontrolled rise in temperature, terminating in the complete oxidation of the reaction mixture by the sulfuric acid. A large volume of sulfur dioxide is evolved, and the reaction mixture is converted into a voluminous, porous, carbon mass. *The progress of the reaction must be watched throughout its complete course and cannot be left unattended.*

9. The reaction is complete when a drop of the mixture on a piece of wet filter paper does not give an orange ring due to the presence of unreacted 3-nitro-4-aminoanisole. If the test is still positive at the end of the heating period, the temperature should be cautiously raised to 125° and heating continued until the test is negative. If the reaction does not go to completion, it is very difficult to remove this unused starting material from

the product and it must be repeatedly decolorized and recrystallized.

10. On cooling, the sulfate salt of the 6-methoxy-8-nitroquinoline partially crystallizes from the reaction mixture. By stirring the mixture, the product comes down as a fine tan, microcrystalline precipitate. This can be isolated and crystallized, but it is more convenient to work it up in the form of the base.

11. These methanol washings remove much of the impurities, especially small amounts of unreacted nitroanisidine, with a minimum loss of product. The solubility of 6-methoxy-8-nitroquinoline in methanol at room temperature is 0.8 g. per 100 g. of solvent and at the boiling point is 4.1 g. per 100 g. of solvent. The solubility in chloroform, on the other hand, is 3.9 g. per 100 g. of solvent at room temperature and 14.2 g. at the boiling point. It is possible to obtain about 12 g. of product by working up these washings, but it is usually not worth the trouble.

12. The 4.5 l. of chloroform used is more than is necessary to dissolve the product, but this amount prevents the difficulties arising from crystallization in the Büchner funnel during filtration.

13. If, during the reaction, the temperature has not been properly regulated, the crystals may require another treatment with decolorizing carbon and crystallization from chloroform.

14. The product may also be recrystallized from hot ethylene dichloride using 300 ml. of solvent for each 100 g. The recovery is 80–90% of 6-methoxy-8-nitroquinoline melting at 160–161°.

15. By the same procedure the submitters have prepared 6-ethoxy-8-nitroquinoline in 70% yield, 8-methoxy-6-nitroquinoline in 68% yield, 6-chloro-8-nitroquinoline in 75% yield, and 6-methoxy-5-bromo-8-nitroquinoline in 69% yield from the properly substituted aromatic amines.

3. Methods of Preparation

6-Methoxy-8-nitroquinoline was first obtained by Schulemann and coworkers [1] by a modification of the Skraup reaction. Various other modifications of this reaction have been used by Magidson,[2] Fourneau,[3] Altman,[4] Brahmachari,[5] Misani and Bogert,[6] and Morgan and Tipson.[7] The modification given here was the best of several tried and is taken from the procedure of Strukov.[8]

[1] Schulemann, Schuenhöfer, and Wingler, Ger. pat. 486,079 [*C. A.*, **24**, 1937 (1930)]. F. Bayer and Co., Brit. pat. 267,457 [*C. A.*, **22**, 1216 (1928)].

[2] Magidson and Strukov, *Arch. Pharm.*, **271**, 359 (1933).

[3] Fourneau, Trefouel, Bovet, and Benoit, *Ann. inst. Pasteur*, **46**, 514 (1931).

[4] Altman, *Rec. trav. chim.*, **571**, 941 (1938).

[5] Brahmachari and Bhattachryee, *J. Indian Chem. Soc.*, **8**, 571 (1931).

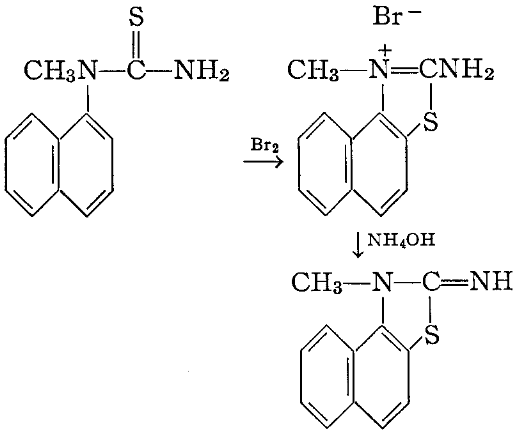
[6] Misani and Bogert, *J. Org. Chem.*, **10**, 347 (1945).

[7] Morgan and Tipson, *J. Am. Chem. Soc.*, **68**, 1569 (1946).

[8] Strukov, *Org. Chem. Ind. U.S.S.R.*, **4**, 523 (1937) [*C. A.*, **32**, 4987 (1938)].

1-METHYL-2-IMINO-β-NAPHTHOTHIAZOLINE

(Naphtho[1,2]thiazole, 1-methyl-1,2-dihydro-2-imino-)



Submitted by Homer W. J. Cressman.
Checked by Nathan L. Drake and Werner R. Boehme.

1. Procedure

In a 1-l. three-necked flask fitted with a thermometer, a dropping funnel, and a mechanical stirrer are placed 65 g. (0.3 mole) of 1-methyl-1-(1-naphthyl)-2-thiourea (p. 58) (Note 1) and

400 ml. of glacial acetic acid (Note 2). To the mechanically stirred suspension, maintained at 18–20° by cooling in a water bath, is added dropwise over a 30-minute period 48 g. (0.3 mole) of bromine in 50 ml. of glacial acetic acid. The light-yellow addition product is stirred an additional 15 minutes at 18–20°. After the thermometer is replaced by an outlet tube (Note 3), the mixture is heated in a water bath maintained at 80–85° (Note 4) for 3 hours. Hydrogen bromide is evolved copiously with the formation of a white, crystalline hydrobromide. When the mixture is cool, it is filtered and the precipitate is washed on the filter with 50 ml. of acetone and then with two 250- to 300-ml. portions of dry ether. One hundred milliliters of concentrated ammonia is then added with stirring to the salt suspended in 700 ml. of warm water (60–65°). The imine base first separates as an oil (Note 5); after the mixture has been stirred and warmed on the steam bath for 10 minutes, it is extracted with 500 ml. of chloroform and filtered by suction through a Norite filter pad 5–6 mm. thick. The bottom layer is separated, washed with 350 ml. of water, and dried by stirring with 40 g. of potassium carbonate. The residual oil, after removal of the solvent on the steam bath under reduced pressure, is poured into an evaporating dish and stirred while cooling. The brownish-colored crystals (Note 6) are dried at 80–85°; they melt at 97–99° and weigh 58–62 g. (90–97%). If desired, the naphthothiazoline (Note 7) can be crystallized from petroleum ether (60–90°) using 75 ml. per gram of product. The recovery of the almost colorless (cream) crystals is 85%. The recrystallized thiazoline melts at 97–99°.

2. Notes

1. The thiazoline was obtained in the best yields and with the lightest color from freshly prepared 1-methyl-1-(1-naphthyl)-2-thiourea. The air-dried thiourea loses hydrogen sulfide and ammonia after several days' storage.

2. The use of glacial acetic acid for cyclization is essential; in chloroform, the bromo-addition product does not lose hydrogen bromide.

3. A gas absorption trap [1] can be used to absorb the hydrogen bromide evolved.

4. The temperature of the water bath is easily maintained at 80–85° by heating it on a steam bath.

5. The oil solidifies on cooling. The crystalline product can be separated by filtration and recrystallized from 50% aqueous alcohol or petroleum ether (60–90°).

6. This product is satisfactory for synthetic purposes.

7. This type of reaction can be used successfully for the preparation of other naphthothiazolines and naphthoselenazolines. The submitter has prepared 2-imino-1-methylnaphtho[1,2]selenazoline, m.p. 94–95°, and 2-imino-1-ethylnaphtho[1,2]selenazoline, m.p. 82–84° by similar methods.

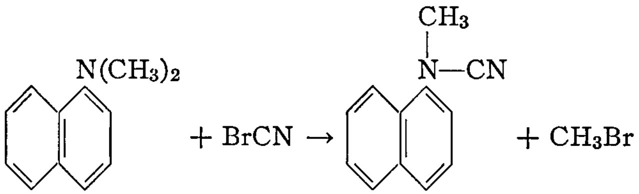
3. Methods of Preparation

The preparation of this compound is not described in the literature.

[1] *Org. Syntheses* Coll. Vol. **2**, 4 (1943).

N-METHYL-1-NAPHTHYLCYANAMIDE

(Cyanamide, methyl-(1-naphthyl)-)



Submitted by Homer W. J. Cressman.
Checked by Nathan L. Drake and Werner R. Boehme.

1. Procedure

Caution! Cyanogen bromide is highly toxic. This preparation should be carried out under a good hood.

A mixture of 171 g. (1 mole) of dimethyl-α-naphthylamine (Note 1) and 125 g. (1.2 moles) of cyanogen bromide [1] in a 1-l. flask (Note 2) is heated under reflux on the steam bath for 16 hours (Note 3). The cooled reaction mixture is added to 2.5 l. of dry ether, and the insoluble quaternary salt (Note 4) is filtered. The ether filtrate is extracted with four 800-ml. portions of approximately 15% hydrochloric acid solution (Note 5) and washed with five 500-ml. portions of water. The ether solution is dried with 30–35 g. of anhydrous calcium sulfate (Drierite). After filtration, the solvent is removed by distillation at atmospheric pressure on the steam bath; the residue is fractionated under reduced pressure. The yield of pale yellow oil, boiling at 170–171°/1 mm. (185–187°/3 mm.), amounts to 115–122 g. (63–67%) (Note 6).

2. Notes

1. Better yields are obtained by dealkylating the tertiary amine in this manner than by starting with the secondary amine. In a similar manner, N-ethyl-1-naphthylcyanamide, b.p. 165–168°/2 mm., is obtained in a 48% yield from diethyl-α-naphthylamine; the yield from the secondary amine is only 25%.

2. Ground-glass equipment is preferable.

3. In order to avoid loss of cyanogen bromide an efficient condenser must be used and the heating should be very gradual at first.

4. About 10 g. of α-naphthyltrimethylammonium bromide, m.p. 160°, is generally obtained.

5. About 25 g. of crystalline dimethyl-α-naphthylamine hydrochloride may be recovered by efficient chilling of the hydrochloric acid extracts.

6. The N-methyl-1-naphthylcyanamide turns dark green upon standing exposed to the air for several days. It may be preserved in sealed, evacuated ampoules in the absence of light.

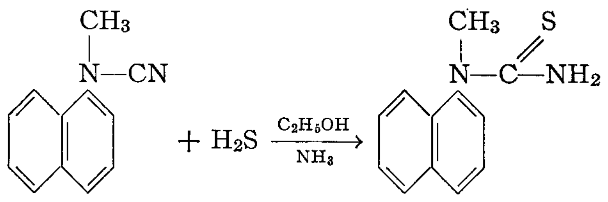
3. Methods of Preparation

The preparation described is based on the method of von Braun and co-workers.[2]

[1] *Org. Syntheses* Coll. Vol. **2**, 150 (1943).
[2] von Braun, Heider, and Muller, *Ber.*, **51**, 281 (1918).

1-METHYL-1-(1-NAPHTHYL)-2-THIOUREA

(Urea, 1-methyl-1-(1-naphthyl)-2-thio-)



Submitted by Homer W. J. Cressman.
Checked by Nathan L. Drake and Werner R. Boehme.

1. Procedure

The apparatus, consisting of a 1-l. three-necked flask, fitted with a glycerol-sealed mechanical stirrer,[1] two inlet tubes (10-mm. bore) extending nearly to the blades of the stirrer, and an outlet tube (Note 1), is set up in a good hood. Into a solution of 91 g. (0.5 mole) of N-methyl-1-naphthylcyanamide (p. 56) in 350 ml. of absolute ethyl alcohol, mechanically stirred and cooled by immersion of the flask in a water bath maintained at 20–25°, ammonia is bubbled at a moderate rate. After 5 minutes, hydrogen sulfide (Note 2) is passed into the solution at about the same rate. The introduction of ammonia is continued for 1.5 hours; hydrogen sulfide is passed into the mixture an additional 30 minutes. A white solid begins to separate soon after the first addition of hydrogen sulfide. After the mixture is chilled in an ice-salt bath, it is filtered. The solid is suspended in 350 ml. of cold water, again separated by filtration, and finally washed with two 100-ml. portions of water, then with two 100-ml. portions of methyl alcohol, and dried. The yield of 1-methyl-1-(1-naphthyl)-2-thiourea, m.p. 168–170° (Note 3), amounts to 89–97 g. (82–90%); this material is suitable for most purposes.

2. Notes

1. The use of an alkali trap [2] is recommended.

2. This general reaction can be used for preparing other unsymmetrical thioureas when the desired cyanamides can be obtained. The submitter has also prepared 1-methyl-1-(1-naphthyl)-2-selenourea, m.p. 174–175° with decomposition, and 1-ethyl-1-(1-naphthyl)-2-selenourea, m.p. 168–170° with decomposition, by substitution of hydrogen selenide for hydrogen sulfide.

3. The thiourea can be further purified by recrystallization from ethanol. The recrystallized product melts at 170–171°.

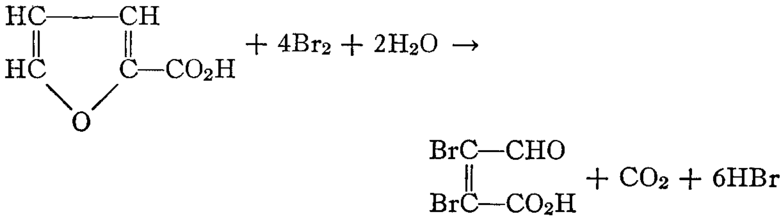
3. Methods of Preparation

The preparation of this compound is not reported in the literature.

[1] *Org. Syntheses*, **21**, 40 (1941).
[2] *Org. Syntheses* Coll. Vol. **1**, 266 (1941).

MUCOBROMIC ACID

(Acrylic acid, α,β-dibromo-β-formyl-)



Submitted by C. F. H. Allen and F. W. Spangler.
Checked by R. L. Shriner and Nicholas J. Kartinos.

1. Procedure

In a 2-l. three-necked round-bottomed flask, equipped with a reflux condenser attached to a gas trap,[1] a dropping funnel, and a mechanical stirrer, are placed 100 g. (0.9 mole) of furoic acid (Note 1) and 440 ml. of water. The flask is immersed in a pan of crushed ice, and 686 g. (220 ml., 4.3 moles) of bromine is placed in the dropping funnel. The stirrer is started, and the bromine is added over a period of about 1 hour with constant stirring and cooling (Note 2). The bromine is decolorized almost immediately at first and then more slowly as the reaction proceeds. The mixture is then heated to boiling and refluxed for 30 minutes. The condenser is removed and the boiling continued for an additional 30 minutes with one neck of the flask open. The mixture is cooled and chilled thoroughly whereupon the mucobromic acid separates and is collected on a filter. The filter cake is removed and thoroughly triturated with a solution of 5 g. of sodium bisulfite in 150 ml. of water (Note 3), and the product is again removed by filtration. After drying in the air the crude product weighs 155–170 g. (67–73%) and melts at 120–122° (cor.).

The mucobromic acid may be recrystallized by solution in

250 ml. of boiling water with the addition of 2 g. of Darco. The hot solution is filtered, and the filtrate is thoroughly chilled in an ice bath. After filtration and drying there is obtained 148–155 g. (64–67%) of white crystals melting at 123–124° (cor.).

2. Notes

1. The furoic acid may be obtained from furfural by means of the Cannizzaro reaction [2] or by oxidation with alkaline potassium permanganate.[3] It is important to purify the furoic acid to a melting point of 131–132°.

2. It is essential that the flask and its contents be well cooled; otherwise the yield is materially decreased.

3. The sodium bisulfite solution removes the color produced by the excess bromine.

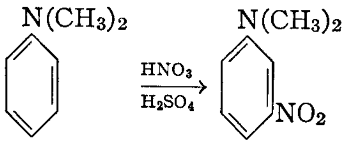
3. Methods of Preparation

The only practical methods of preparation are the action of bromine on furfuraldehyde [4] or furoic acid [5,6,7] in aqueous solution.

[1] *Org. Syntheses* Coll. Vol. **2**, 4 (1943).
[2] *Org. Syntheses* Coll. Vol. **1**, 276 (1941).
[3] Wagner and Simons, *J. Chem. Education*, **13**, 270 (1936).
[4] Simonis, *Ber.*, **32**, 2085 (1899).
[5] Jackson and Hill, *Am. Chem. J.*, **3**, 41 (1881–2); *Ber.*, **11**, 1671 (1878).
[6] Schmelz and Beilstein, *Ann. Suppl.*, **3**, 276 (1864).
[7] Limpricht, *Ann.*, **165**, 293 (1873).

m-NITRODIMETHYLANILINE

(Aniline, N,N-dimethyl-*m*-nitro-)



Submitted by HOWARD M. FITCH.
Checked by C. F. H. ALLEN and J. A. VANALLAN.

1. Procedure

In a 3-l. three-necked round-bottomed flask fitted with an effective mechanical stirrer, a dropping funnel, and a thermometer, and surrounded by an ice bath, is placed 1270 ml. (23.0 moles) of concentrated sulfuric acid (sp. gr. 1.84). Then 363 g. (3.0 moles) of dimethylaniline (Note 1) is slowly added with stirring and cooling so that the temperature remains below 25°. Stirring and cooling are continued until the temperature falls to 5°. A nitrating mixture is prepared by adding 366 g. (200 ml., 3.6 moles) of concentrated sulfuric acid (sp. gr. 1.84) to 286 g. (200 ml., 3.15 moles) of concentrated nitric acid (sp. gr. 1.42), with cooling and stirring. This is placed in the dropping funnel and added, drop by drop, the end of the dropping funnel being kept beneath the surface of the solution of dimethylaniline sulfate. The temperature is regulated between 5° and 10°, best by addition of small pieces of Dry Ice (Note 2); about 1.5 hours is required (Note 3). When the addition has been completed, the solution is stirred at 5–10° for 1 hour, and then poured, with stirring (Note 4), into an enameled pail containing 6 l. of ice and water (Note 5). Concentrated ammonium hydroxide is added slowly, with good stirring and using a dropping funnel that extends beneath the surface of the liquid, until the color of the precipitate changes to a light orange (Note 6). During this step the temperature is kept below 25°, using Dry Ice. From 1900 to

2050 ml. of ammonium hydroxide is required. The crude *p*-nitrodimethylaniline is collected on a filter and washed with 200 ml. of water (Note 7). Concentrated ammonium hydroxide (sp. gr. 0.90) is again added to the combined filtrate and washings, with good agitation and cooling to keep the temperature below 25°, until the liquid gives a purple color on Congo red paper (Note 8). From 1500 to 1650 ml. of ammonium hydroxide is required. The product is collected on a Büchner funnel and washed with 500 ml. of water. The crude *m*-nitrodimethylaniline (316–342 g. dry weight) is recrystallized from 400 ml. of hot 95% ethanol and carefully washed on the filter with 100 ml. of cold 95% ethanol. The yield is 280–316 g. (56–63%) of bright orange crystals that melt at 59–60°.

2. Notes

1. The dimethylaniline should be of good quality. Dimethylaniline (free from mono), m.p. 1°, of the Eastman Kodak Company, and dimethylaniline, Merck, are satisfactory.

2. A cooling bath of Dry Ice and acetone can be used, but addition of the solid directly to the mixture is more satisfactory and less is required.

3. The mixture may be left overnight at room temperature. It is advisable to complete the subsequent neutralization in one day.

4. A powerful stirrer is required to mix the large volumes.

5. If large equipment is not available, it is convenient to divide the nitration mixture into four parts (about 490 ml. each) and to pour each portion into 1.5 l. of ice and water in a 4-l. beaker. After neutralization, the precipitates from the four lots are combined on the filter.

6. It is essential that all the *para* isomer be precipitated, since it is not easily removed by recrystallization from solvents. The point at which the yellow *p*-nitrodimethylaniline ceases to precipitate and the orange *m*-nitrodimethylaniline begins to precipitate is difficult to judge without experience, since the solution itself has an orange color. If doubt exists, a small sample

may be filtered so that the color of the precipitate can be clearly seen. If very much of the *para* isomer remains in solution, a yellow precipitate or turbidity is obtained on diluting the filtrate with several volumes of water.

7. If the *para* isomer is to be recovered, the precipitate should be washed well with water to remove all acid and dried. The solid (143–155 g.) is recrystallized from 400 ml. of benzene and carefully washed on the filter with 125 ml. of cold benzene. The yield is 74–92 g. (14–18%) of bright yellow crystals that melt at 163–164°.

8. Substantially all the *m*-nitrodimethylaniline is precipitated at a *p*H of about 3, while any dimethylaniline present remains in solution.

3. Methods of Preparation

The above procedure is a modification of the method of Groll;[1] a more laborious method of purification has been described.[2] *m*-Nitrodimethylaniline can also be prepared by methylation of *m*-nitroaniline using methyl sulfate.[3]

[1] Groll, *Ber.*, **19**, 198 (1886).
[2] Bobranskiĭ and Eker, *J. Applied Chem. U.S.S.R.*, **14**, 524 (1941) [*C. A.*, **36**, 3159 (1942)].
[3] Ullmann, *Ann.*, **327**, 112 (1903).

3-PENTEN-2-OL

$$CH_3Cl + Mg \xrightarrow{\text{Ether}} CH_3MgCl$$

$$CH_3CH{=}CHCHO + CH_3MgCl \rightarrow$$

$$CH_3CH{=}CHCH(OMgCl)CH_3 \xrightarrow[NH_4Cl]{H_2O}$$

$$CH_3CH{=}CHCHOHCH_3 + MgCl_2 + NH_4OH$$

Submitted by E. R. Coburn.
Checked by Homer Adkins, B. W. Winner, John Woods, R. F. McElwee and Robert M. Ross.

1. Procedure

A 5-l. round-bottomed three-necked flask is equipped with a mechanical stirrer in a suitable seal (Note 1), a reflux condenser of the cold finger type (Note 2) protected from moisture in the air by a drying tube, and a gas delivery tube extending nearly to the bottom of the flask. The flask is surrounded by an ice bath, and the cold finger is filled with solid carbon dioxide in acetone. Approximately 1700 ml. of dry ether and 61 g. (2.5 gram atoms) of magnesium are placed in the flask and cooled to about 0°. Methyl chloride (130 ml., 130 g., 2.6 moles) is condensed (Note 3) in a 250–300 ml. test tube held in a bath of solid carbon dioxide in acetone (Note 4). About 50 ml. of methyl chloride is allowed to distil from the test tube containing the methyl chloride through the gas delivery tube into the rapidly stirred mixture of ether and magnesium. The reaction mixture is then warmed until the reaction of methyl chloride and magnesium is under way. A crystal of iodine may be added if the reaction does not start readily. The methyl chloride is then allowed to distil into the reaction mixture during a period of about 3 hours. The reaction mixture and the tube containing the methyl chloride are cooled if the refluxing of the reaction mixture becomes so vigorous that the reflux condenser does not condense the methyl chloride. After all the methyl chloride has been

added, the reaction mixture is warmed for 1 hour so that there is a gentle reflux.

At the end of this time, when almost all the magnesium has reacted, the Dry Ice cold finger is replaced with a water condenser and the gas delivery tube with a dropping funnel. A solution of 142 g. (2.02 moles) of freshly distilled crotonaldehyde in 300 ml. of dry ether is added dropwise while the reaction mixture is stirred vigorously and cooled. The reaction mixture is allowed to stand at room temperature for 1 hour.

The Grignard addition compound is decomposed by adding 435 ml. of a saturated ammonium chloride solution (Note 5) dropwise, with vigorous stirring, to the thoroughly cooled reaction mixture. A dense white precipitate, too heavy to be stirred mechanically, forms and settles to the bottom of the flask. After the reaction mixture has been allowed to stand for 1 hour, the ether solution is poured off and the precipitate washed by decantation with two 300-ml. portions of ether.

The ether is removed by distillation, and the residual 3-penten-2-ol is distilled through a short column (Note 6) at atmospheric pressure. The yield of material boiling at 119–121° is 140–150 g. (81–86%). Pure 3-penten-2-ol boils at approximately 120°/740 mm.

2. Notes

1. A Hershberg type of stirrer [1] is preferred. The submitter used a stirrer of tantalum with a mercury seal; the checkers used a Nichrome stirrer in a simple rubber seal.[2]

2. The reflux condenser must be of very high capacity, as otherwise methyl chloride may be lost. The checkers used a cold finger type of condenser in which the dimensions of the finger or container for the refrigerant were 30 cm. in length and 3 cm. in outside diameter. The glass jacket surrounding the finger was 4.5 cm. in outside diameter, but was drawn down to 1.3 cm. below the finger for convenience of insertion into one of the necks of the reaction flask.

3. Methyl chloride is led from a commercial cylinder to the bottom of the test tube used for measuring and storing the

reagent. The tube is previously marked so that the desired volume (130 ml.) of methyl chloride may be readily measured.

4. The checkers also obtained equally good results with less effort by allowing a slow stream of dry methyl chloride to pass directly from the commercial cylinder into the reaction mixture until practically all the magnesium had reacted.

5. Hydrolysis of the Grignard complex with saturated ammonium chloride solution possesses the advantage that the resulting ethereal solution of the alcohol is neutral and sufficiently dry so that it need not be dried before distillation. The alcohol is dehydrated if it is distilled from a mixture containing even a trace of a mineral acid. Approximately 125 g. of ammonium chloride and 345 ml. of water are required for the saturated solution referred to above.

6. The submitter used a Hempel column. The checkers used a modified Widmer or Vigreux column, 1.3 cm. in diameter and 15 cm. in length.

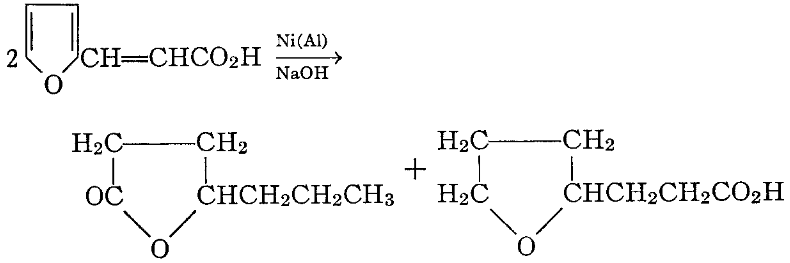
3. Methods of Preparation

3-Penten-2-ol has been prepared by the addition of methyl magnesium iodide [3,4] or bromide [5,6,7,8] to crotonaldehyde and by the partial dehydration of pentandiol.[9]

[1] *Org. Syntheses* Coll. Vol. **2**, 117 (1943).
[2] *Org. Syntheses*, **21**, 40 (1941).
[3] Courtot, *Bull. soc. chim.*, (3), **35**, 983 (1906).
[4] Kyriakides, *J. Am. Chem. Soc.*, **36**, 663 (1914).
[5] Reif, *Ber.*, **39**, 1603 (1906); **41**, 2739 (1908).
[6] Mulliken, Wakeman, and Gerry, *J. Am. Chem. Soc.*, **57**, 1605 (1935).
[7] Auwers and Westermann, *Ber.*, **54**, 2996 (1921).
[8] Hurd and Cohen, *J. Am. Chem. Soc.*, **53**, 1917 (1931).
[9] Kyriakides, *J. Am. Chem. Soc.*, **36**, 996 (1914).

γ-*n*-PROPYLBUTYROLACTONE and β-(TETRAHYDROFURYL)-PROPIONIC ACID

(Enanthic acid, γ-hydroxy-, lactone, and 2-furanpropionic acid, tetrahydro-)



Submitted by ERWIN SCHWENK, DOMENICK PAPA, HILDA HANKIN, and HELEN GINSBERG.
Checked by CLIFF S. HAMILTON and FLAVEN E. JOHNSON.

1. Procedure

In a 2-l. beaker resting on a hot plate and equipped with a mechanical stirrer are placed 150 g. of sodium hydroxide (Note 1) dissolved in 800 ml. of water and 41.4 g. (0.3 mole) of furylacrylic acid.[1] The stirrer is started, and to the warm solution (Note 2) 100 g. of Raney nickel-aluminum alloy is added, in small portions, over a period of 4–4.5 hours (Notes 3 and 4). During the addition of the alloy, the temperature of the mixture is kept at 60–70° and then is raised to approximately 95° where it is held for an additional 2–3 hours, with stirring. From time to time sufficient water is added to the reaction mixture to maintain approximately the original volume. The hot solution is filtered by decantation, and the nickel residue (Note 5) is washed with two 50-ml. portions of hot 2% sodium hydroxide solution. The combined filtrates and washings are cooled and then immediately added slowly (Note 6), with good stirring, to 800 ml. of concentrated hydrochloric acid (Note 7). The solution at this point

is strongly acid to Congo red paper (Note 8). The acidified solution is cooled and thoroughly extracted with three 200-ml. portions of ether (Note 9). The ether extracts are combined and washed once with 100 ml. of 10% sodium chloride solution, the ether is evaporated, and the residue is fractionally distilled in a modified Claisen flask. The yield of γ-*n*-propylbutyrolactone boiling at 84–85°/5 mm., n_D^{25} 1.4385, is 13.0–14.9 g. (33–37%), while the yield of β-(tetrahydrofuryl)-propionic acid boiling at 123–124°/5 mm., n_D^{25} 1.4578, is 15.0–17.0 g. (34–39%) (Notes 10, 11).

2. Notes

1. Solid sodium hydroxide is used in order to take advantage of the heat of solution. If the mixture at this stage is allowed to cool, it will be necessary to heat the solution to 50–60° before the addition of the alloy is begun.

2. Some of the furylacrylic acid remains undissolved but goes into solution readily after the addition of the nickel-aluminum alloy is begun.

3. If any excessive frothing occurs during the addition of the alloy, a few drops of octyl alcohol can be added from time to time.

4. During the addition of the alloy, it is advantageous to stir the solution efficiently, the alloy being added in the vortex of the solution. If the addition of the alloy is made on the surface of the liquid, most of the hydrogen developed is lost without entering into the reaction.

5. The Raney nickel residue is quite active and will ignite if allowed to become dry. It may readily be disposed of by pouring into dilute mineral acid. This nickel residue is sufficiently active for various types of catalytic hydrogenations requiring the use of Raney nickel catalyst.

6. If the acidified mixture is allowed to become too hot, some of the material may be lost by steam distillation.

7. The alkaline solution is added to the hydrochloric acid in the manner described, since the reverse order of addition usually results in the precipitation of aluminum salts which dissolve only

after considerable heating and stirring. The alkaline solution is added at such a rate that at no time is there any appreciable amount of solid present.

8. If insufficient hydrochloric acid is used at this stage, aluminum salts will precipitate and will make the ether extractions difficult because of the formation of emulsions.

9. The acidified solution has also been extracted with ether in a continuous liquid-liquid extractor, this extraction requiring approximately 20 hours. Only slightly higher yields of the two products are obtained by this modification.

10. According to the submitters an alternative procedure for the separation of γ-*n*-propylbutyrolactone and β-(tetrahydrofuryl)-propionic acid is the following:

The ether extracts, after washing with salt solution, are extracted with one 100-ml. and two 50-ml. portions of 5% sodium carbonate solution. It is important that the ether solution be free of any mineral acid before the carbonate extractions are made. The residual ether solution, after being washed with 10% sodium chloride solution, is dried over sodium sulfate. The ether is removed by distillation, and the residue is distilled under reduced pressure. The yield of γ-*n*-propylbutyrolactone is 14.5 g. (36%), b.p. 78–80°/2 mm. The combined sodium carbonate extracts are acidified to Congo red paper with concentrated hydrochloric acid and then thoroughly extracted with one 100-ml. and two 50-ml. portions of ether. The combined ether extracts are washed with 10% sodium chloride solution and dried; and, after the ether is removed by distillation, the residue is distilled under reduced pressure. The yield of β-(tetrahydrofuryl)-propionic acid is 15.9 g. (36%), b.p. 118–120°/2 mm.

11. The submitters have used this procedure for the reduction of β-(α-thenoyl)-propionic acid [2] from which ω-hydroxycaprylic acid [3] has been obtained in a yield of 38%, melting at 54–55°, and δ-*n*-propylvalerolactone in a yield of 31%, boiling at 116–117°/10 mm.

3. Methods of Preparation

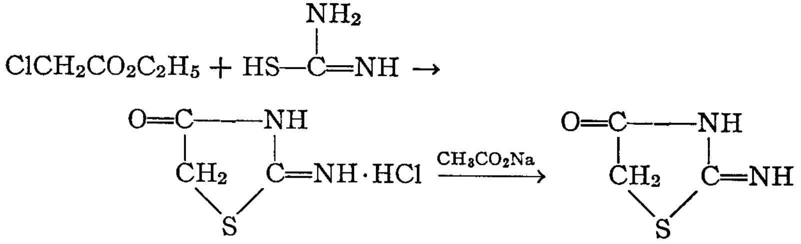
γ-*n*-Propylbutyrolactone has been obtained from γ-bromoenanthic acid on boiling with water,[4] from β,γ-hepteneoic acid and sulfuric acid,[5] and by distilling γ-propylparaconic acid.[6]

β-(Tetrahydrofuryl)-propionic acid has been obtained from furylacrylic acid by catalytic reduction with platinum oxide,[7] with nickel on kieselguhr,[8] or with palladium black.[9]

[1] *Org. Syntheses*, **25**, 51 (1945).
[2] Fieser and Kennelly, *J. Am. Chem. Soc.*, **57**, 1615 (1935).
[3] Chuit and Hausser, *Helv. Chim. Acta*, **12**, 466 (1929).
[4] Fittig and Schmidt, *Ann.*, **255**, 80 (1889).
[5] Rupe, *Ber.*, **35**, 4272 (1902).
[6] Fittig, *Ann.*, **255**, 76 (1889).
[7] Kaufmann and Adams, *J. Am. Chem. Soc.*, **45**, 3042 (1923).
[8] Burdick and Adkins, *J. Am. Chem. Soc.*, **56**, 440 (1934).
[9] Windaus and Dalmer, *Ber.*, **53**, 2304 (1920).

PSEUDOTHIOHYDANTOIN

(4-Thiazolidone, 2-imino-)



Submitted by C. F. H. Allen and J. A. VanAllan.
Checked by H. R. Snyder and Frank X. Werber.

1. Procedure

In a 1-l. flask surmounted by a reflux condenser, 76 g. (1 mole) of thiourea, m.p. 174–176°, is dissolved in 500 ml. of 95% ethanol by refluxing for 10–15 minutes. Then 125 g. (108 ml., 1.02 moles) of ethyl chloroacetate is added slowly (15–20 minutes) through the

condenser while gentle refluxing is continued. After the mixture has been refluxed for 3 hours longer, it is allowed to cool to room temperature and the solid is filtered by suction on a 14-cm. Büchner funnel. The filtrate is used to rinse any solid adhering to the walls of the reaction flask onto the filter. The crude product is pressed down firmly and washed with 50 ml. of ethanol (Note 1).

The crude hydrochloride is dissolved in 1200 ml. of hot, freshly boiled water (Note 2) in a 2-l. beaker, a boiling solution of 121 g. of sodium acetate trihydrate in 150 ml. of water is added, and the mixture is heated to boiling (Note 3). The resulting clear solution is stored in the ice chest overnight. The crystalline pseudothiohydantoin is filtered and dried to constant weight at 60°. The product weighs 92–95 g. (79–82%). A reproducible decomposition point of 255–258° can be determined with the aid of a melting-point bar (Note 4).

2. Notes

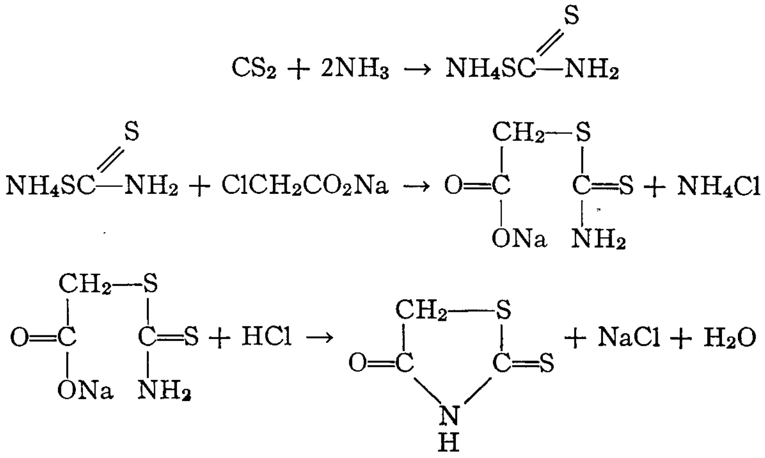
1. The yield of the crude hydrochloride, dried to constant weight, is about 126 g.; the decomposition range is 210–255°.
2. The water is boiled before use to expel dissolved oxygen, the presence of which in the solution may cause the final product to have a yellow color.
3. Prolonged boiling should be avoided, as hydrolysis of the imino group occurs very easily. When sodium carbonate is substituted for sodium acetate the yield drops 10%.
4. The decomposition point as measured in the ordinary manner varies with the temperature of the bath at the time of the introduction of the sample. When the melting-point bath is heated so that the temperature rises by 2° per minute, a sample introduced just as the temperature reaches 200° develops an observable brown color at 206° and then darkens so rapidly that no liquid phase can be identified; if, under the same conditions, the sample is introduced when the bath temperature is 238° the decomposition begins immediately but a liquid phase can be recognized when the bath temperature is in the range 241–243°.

3. Methods of Preparation

Pseudothiohydantoin has been obtained from thiourea and ethyl chloroacetate [1] and from thiourea and chloroacetic [2,3] or dichloroacetic acids.[4]

[1] Klason, *Ber.*, **10**, 1352 (1877).
[2] Andreasch, *Monatsh.*, 8, 424 (1887).
[3] Schmidt, *Arch. Pharm.*, **258**, 229 (1920).
[4] Dixon, *J. Chem. Soc.*, **63**, 816 (1893).

RHODANINE



Submitted by C. Ernest Redemann, Roland N. Icke, and Gordon A. Alles.
Checked by H. R. Snyder and John H. Johnson.

1. Procedure

A. *Ammonium dithiocarbamate.* Gaseous ammonia is passed into 250 ml. of 95% ethanol (Note 1) contained in a 1-l. Erlenmeyer flask immersed in an ice bath until the gain in weight is 39 g. (2.3 moles). To this solution, still cooled by the ice bath, is added a well-cooled mixture of 76 g. (60 ml., 1 mole) of carbon

disulfide and 200 ml. of ether. The flask is stoppered loosely (Note 2) and allowed to remain in the ice bath for 2 or 3 hours and then at room temperature overnight (Note 3). The mixture is again cooled in an ice bath or refrigerator, and the crystals are collected by filtration (hood!), sucked dry, and washed on the filter with two 50-ml. portions of ether. Air is drawn through the crystals for 5 minutes (Note 4) to effect removal of most of the ether. The product is used promptly without further treatment; the weight of the lemon-yellow solid varies between 80 and 90 g., depending principally on the completeness of the removal of the solvent.

B. *Rhodanine.* Just before the filtration of the ammonium dithiocarbamate, a solution of sodium chloroacetate is prepared by dissolving 71 g. (0.75 mole) of chloroacetic acid in 150 ml. of water contained in a 1-l. wide-mouth round-bottomed flask and neutralizing the acid with 40 g. (0.38 mole) of anhydrous sodium carbonate (or an equivalent amount of the hydrate) while stirring the solution mechanically. This solution is cooled in an ice bath, and the ammonium dithiocarbamate from the preceding preparation is added during 5 minutes with continual stirring. As soon as the first portion of ammonium dithiocarbamate is added the solution becomes very dark in color. After all the dithiocarbamate has been added the ice bath is removed and stirring is discontinued. The solution is allowed to stand for 20–30 minutes longer, during which time the color changes to a clear yellow. In a 1-l. beaker 400 ml. of 6 *N* hydrochloric acid is heated to boiling, and the above solution (Note 5) is poured slowly with stirring into the hot acid. Heating is continued until the solution has attained a temperature of 90–95°, after which the solution is allowed to cool slowly to room temperature. The rhodanine separates as nearly colorless long blades which are collected by filtration, washed well with water, and dried. The product weighs 83–89 g. (83–89%, based on the chloroacetic acid), and melts at 167–168°. Recrystallization from boiling glacial acetic acid (2 ml. per gram) raises the melting point to 168–168.5° (Note 6); the recovery, without reworking of the mother liquor, is 87%.

2. Notes

1. Absolute ethanol is satisfactory. Methanol may be used, but ammonium dithiocarbamate is much more soluble in methanol than in ethanol and the recovery will be lower.

2. The flask should be stoppered loosely to retard the escape of ammonia. It is not wise to stopper it tightly, as some gas is evolved and pressure may develop. Hydrogen sulfide is present in the gases evolved.

3. The success of the preparation depends upon securing ammonium dithiocarbamate of good quality. Although much solid sometimes separates within 1 or 2 hours, it contains a large amount of the very unstable ammonium trithiocarbamate.[1] After prolonged standing, the solid is nearly pure ammonium dithiocarbamate.

4. Ammonium dithiocarbamate is relatively unstable, and no attempt should be made to dry the compound thoroughly before use.

5. If this solution is not clear and free from solid impurities it should be filtered before addition to the acid.

6. The melting points observed with the aid of a hot-stage microscope are slightly higher—170–170.5° for the unrecrystallized material, and 170.5–171° for the purified product. Although rhodanine usually is described in the literature as melting with decomposition, the checkers observed no evidence of decomposition during melting under the microscope and found the melting point unchanged when molten samples in ordinary melting-point tubes were cooled and remelted.

3. Methods of Preparation

Rhodanine has been prepared by the reaction of chloroacetic acid with ammonium thiocyanate;[2] by the action of ethyl chloroacetate upon ammonium dithiocarbamate in the presence of alcohol and hydrogen chloride;[3] by saturating a solution of thioglycolic acid and potassium thiocyanate in absolute alcohol with hydrogen chloride;[4] by ring closure of thiocarbamylthio-

glycolic acid in various ways.[5,6,7] The present method of preparation is adapted from that of Julian and Sturgis.[7]

[1] Miller, *Contrib. Boyce Thompson Inst.*, **5**, 31 (1933).
[2] Nencki, *J. prakt. Chem.*, (2) **16**, 2 (1877).
[3] Miolati, *Ann.*, **262**, 85 (1891).
[4] Fredyl, *Monatsh.*, **10**, 82 (1889).
[5] Holmberg, *Ber.*, **39**, 3069 (1906); *J. prakt. Chem.*, (2) **79**, 261, 265 (1909).
[6] Granacher, *Helv. Chim. Acta*, **5**, 152 (1920).
[7] Julian and Sturgis, *J. Am. Chem. Soc.*, **57**, 1126 (1935).

STEAROLIC ACID

$$CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2CH_3 + Br_2 \rightarrow CH_3(CH_2)_7CHBrCHBr(CH_2)_7CO_2CH_3$$

$$CH_3(CH_2)_7CHBrCHBr(CH_2)_7CO_2CH_3 + 3KOH \rightarrow CH_3(CH_2)_7C{\equiv}C(CH_2)_7CO_2K + CH_3OH + 2KBr + 2H_2O$$

$$CH_3(CH_2)_7C{\equiv}C(CH_2)_7CO_2K + HCl \rightarrow CH_3(CH_2)_7C{\equiv}C(CH_2)_7CO_2H + KCl$$

Submitted by Homer Adkins and R. E. Burks, Jr.
Checked by Arthur C. Cope and Harold R. Nace.

1. Procedure

Bromine is added dropwise with stirring to 35 g. (0.118 mole) of methyl oleate (Note 1) in a 500-ml. round-bottomed flask. The mixture is kept below 50° throughout the addition, which is continued until a slight excess of bromine is present; approximately the theoretical amount (18.9 g.) is decolorized. Methyl oleate (2 or 3 drops) is then added until the bromine color just disappears. *n*-Amyl alcohol (50 ml.) (Note 2) and potassium hydroxide pellets (40 g., 0.61 mole assuming 85% purity) are added to the flask, and the mixture is heated under reflux for 4 hours in an oil bath at 150°. Then approximately 50 ml. of the *n*-amyl alcohol is distilled at atmospheric pressure (Note 3). The residue on cooling solidifies into a tan-colored mass. Phenolphthalein is added as an indicator, the mixture is cooled in an ice bath, and concentrated hydrochloric acid is added in portions until the red color disappears but reappears on stirring of the viscous mass. This process is continued until the mixture remains colorless. Water (approximately 200 ml.) is added, and the mixture is allowed to come to room temperature. Concentrated hydrochloric acid is added until the mixture is acid to methyl orange. The mixture is again cooled in an ice bath; the oily layer solidifies into a wax, and the acidic water solution is decanted. The wax is dissolved in 100 ml. of 95% ethanol at room temperature, and water is added until the solution becomes turbid. The mixture is heated on a steam bath until a clear solution is formed, and then it is cooled in an ice bath and stirred while the product crystallizes. The semisolid mass is filtered, and the product is recrystallized three times from an alcohol-water mixture. After drying in a vacuum desiccator the yield is 11–14 g. (33–42%), m.p. 46–46.5°; neutral equivalent 279.7–281.4 (calcd. 280.4); hydrogen absorbed by catalytic reduction 94–100%.

2. Notes

1. The methyl oleate was prepared by esterification [1] of commercial U.S.P. grade oleic acid and fractionated through a Widmer column. The fractions used boiled at 140–144° (0.5 mm.), 175–179° (2 mm.), and had n_D^{25} 1.4500–1.4527 and an iodine number of 93–97 (calcd. 85.6) by iodine bromide titration.[2]

2. *n*-Amyl alcohol was selected as a solvent with a convenient boiling point for the dehydrohalogenation. Acetylenic triple bonds are attacked by water in the presence of strong alkali or strong acid.

3. Part of the dehydrohalogenation occurs during the distillation of *n*-amyl alcohol at atmospheric pressure. If the solution was concentrated by distillation under reduced pressure, the product contained bromine and failed to crystallize.

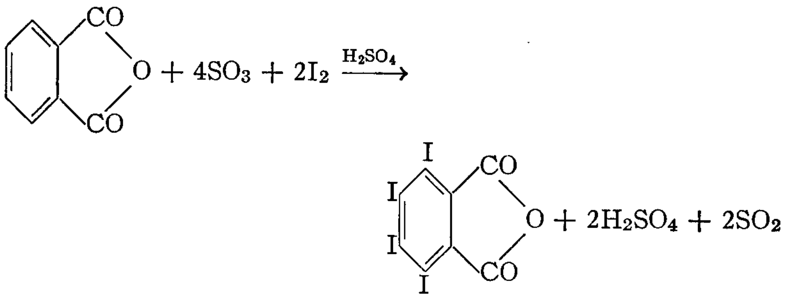
3. Methods of Preparation

Stearolic acid has been prepared by the dehydrohalogenation of brominated olive or almond oil,[3] dibromostearic acid,[4] or dichlorostearic acid.[5] The procedure described is a modification of one used by Kino.[4]

[1] Skraup and Schwamberger, *Ann.*, **462**, 155 (1928).
[2] Mahin, *Quantitative Analysis*, 4th ed., pp. 416–420, McGraw-Hill Book Co., New York, 1932.
[3] Hoffmann-La Roche, Ger. pat. 243,582 [*Chem. Zentr.*, **1912**, I, 695].
[4] Kino, *J. Soc. Chem. Ind. Japan*, **32**, 187 (1929) [*C. A.* **24**, 1998 (1930)].
[5] Inoue and Suzuki, *Proc. Imp. Acad. Tokyo*, **7**, 261 (1931) [*C. A.*, **26**, 87 (1932)].

TETRAIODOPHTHALIC ANHYDRIDE

(Phthalic anhydride, tetraiodo-)



Submitted by C. F. H. Allen, Homer W. J. Cressman, and H. B. Johnson.
Checked by H. R. Snyder and E. Van Heyningen.

1. Procedure

In a 3-l. three-necked flask with ground-glass joints are placed 148 g. (1.0 mole) of phthalic anhydride, 324 g. (60% of the total of 2.12 moles to be added) of iodine, and 600 ml. of 60% fuming sulfuric acid. The flask, fitted with an air condenser 90 to 100 cm. in length (Note 1), is arranged for heating by a water bath. A tube leads from the condenser to a gas trap.[1]

The temperature of the water bath is raised cautiously to 45–50°, at which point the reaction begins (Note 2). Heating is continued until visible reaction has almost completely stopped. During this time (Note 3), the temperature has been raised gradually to 65°. The flask is then cooled by flooding the bath with ice water, and a second portion, 162 g. (30% of the total), of iodine is added. The flask is heated again at 65° until the reaction ceases. After cooling as before, the last portion, 54 g. (10% of the total), of iodine is added.

When reaction at 65° has ceased and the flask has been cooled, the condenser is removed, and the flask is arranged for heating on an oil bath in a well-ventilated area (Note 4). The temperature of the bath is raised to 175° and maintained at 170–180° until the evolution of sulfur trioxide and iodine fumes has slowed considerably (about 2 hours at 170°). The flask is allowed to cool to about 60° before the contents are poured into a beaker, which is allowed to stand overnight at room temperature.

The solid is filtered by suction on a glass filter cloth and is washed with two 100-ml. portions of concentrated sulfuric acid and then with three 200-ml. portions of water (Note 5). The light yellow crystalline material is then transferred to a 3-l. beaker where it is stirred for 30 minutes with a solution of 20 g. of sodium bisulfite in 1500 ml. of water to remove the last traces of iodine. The heavy solid is allowed to settle to the bottom of the beaker, and the bisulfite solution is poured off. The crystals are washed with three 1-l. portions of water, each portion being decanted as before (Note 6), and then are transferred to a funnel. The product is washed with an additional 1-l. portion of water and two 200-ml. portions of acetone and dried in an oven at 60°. The product amounts to 520–535 g. (80–82% based on the phthalic anhydride) (Notes 7 and 8) and melts at 327–328° (Note 9).

2. Notes

1. A water-cooled condenser maintained at 20–25° may be used.

2. Temporary cooling by cold water may be necessary to keep the reaction in check. It must be closely watched at this stage.

3. The lengths of the periods of heating are approximately 5, 3, and 1 hour, respectively. In a run of one-half the size described, the checkers found the periods required to be about 4, 1.5, and 1 hour, respectively.

4. This operation is carried on most conveniently out-of-doors. For the 0.5-mole run, the checkers fitted the flask to the gas trap with a U-tube of 2-cm. bore, having a ground-glass joint for the connection to the flask. The large-diameter tube permitted the operation to be carried out in a hood with no danger of clogging of the apparatus by sublimed iodine.

5. This method of working up the product is superior to the usual one of pouring on ice in that a purer material is obtained and a difficult recrystallization is thus avoided.

6. Some impurities tend to float and are removed with the wash water.

7. It was observed that sunlight or illumination by a photoflood lamp tended to make the reaction more vigorous but did not produce any significant increase in yield.

8. Yields of the same order were obtained starting with 0.5, 1.0, and 10.0 moles of phthalic anhydride. In the runs with 10.0 moles of phthalic anhydride, a greater excess of iodine was found necessary; i.e., the weights of iodine added were 3240 g., 1620 g., 540 g., 500 g., 300 g. The length of the heating periods were approximately 72, 48, 24, 24, and 12 hours, respectively.

9. The melting point may vary from 325° to 332° but usually falls within a two-degree range. No suitable solvent for recrystallization has been found. The recrystallized product always has a lower melting point than the original material.

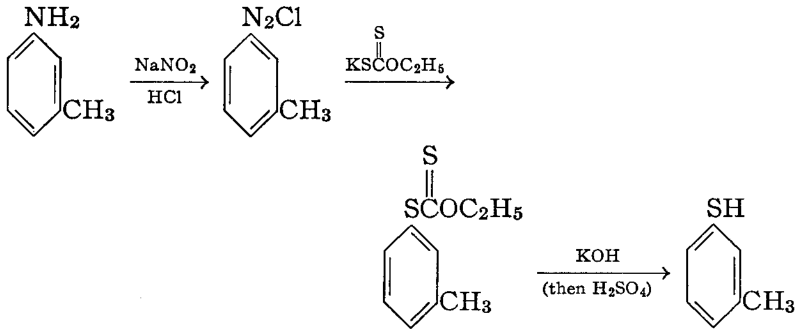
3. Methods of Preparation

The method given is the only satisfactory one so far reported.[2,3,4,5]

[1] *Org. Syntheses* Coll. Vol. **2**, 4 (1943).
[2] Juvalta, Ger. pat. 50, 177 [*Frdl.*, **2**, 94 (1887–1890)].
[3] Rupp, *Ber.*, **29**, 1634 (1896).
[4] Pratt and Shupp, *J. Am. Chem. Soc.*, **40**, 254 (1918).
[5] Perkins and Quimba, *Am. J. Pharm.*, **106**, 467–473 (1934).

m-THIOCRESOL

(*m*-Toluenethiol; *m*-tolyl mercaptan)



Submitted by D. S. Tarbell and D. K. Fukushima.
Checked by C. F. H. Allen and John R. Byers, Jr.

1. Procedure

All the steps in this preparation, including sealing the product in bottles or ampoules, should be carried out under a good hood. Care should be exercised to avoid contact with m-thiocresol or its solutions since it is a skin irritant.

In a 1-l. flask, equipped with a mechanical stirrer and thermometer for reading low temperatures, and immersed in an ice bath, are placed 150 ml. of concentrated hydrochloric acid (sp. gr. 1.18) and 150 g. of crushed ice. The stirrer is started, and 80 g. (0.75 mole) of *m*-toluidine (b.p. 92–93°/15 mm.) is slowly added. The mixture is cooled to 0°, and a cold solution of 55 g. (0.8 mole) of sodium nitrite in 125 ml. of water is slowly added, the temperature being kept below 4°.

In a 2-l. flask equipped with a thermometer, dropping funnel, and stirrer is placed a solution of 140 g. of potassium ethyl xanthate (Note 1) in 180 ml. of water. This mixture is warmed to 40–45° and kept in that range during the slow addition of the cold diazonium solution (Note 2); about 2 hours is required

(Note 3). After an additional 30 minutes at this temperature to ensure complete decomposition of the intermediate compound, the red, oily *m*-tolyl ethyl xanthate is separated and the aqueous layer is extracted twice, using 100-ml. portions of ether. The combined oil and extracts are washed once with 100 ml. of 10% sodium hydroxide solution (Note 4) and then with several portions of water until the washings are neutral to litmus. The ether solution is dried over 25 g. of anhydrous calcium chloride, and the ether is removed by distillation. The crude residual *m*-tolyl ethyl xanthate is dissolved in 500 ml. of 95% ethanol, the solution brought to boiling, and the source of heat removed. To this hot solution is added slowly 175 g. of potassium hydroxide pellets so that the solution keeps boiling, and the mixture is refluxed until a sample is completely soluble in water (about 8 hours). Approximately 400 ml. of alcohol is then removed by distillation on a steam bath, and the residue is taken up in the minimum of water (about 500 ml.). The aqueous solution is extracted with three 100-ml. portions of ether, the extract being discarded. The aqueous solution is now made strongly acid to Congo red paper, using 6 *N* sulfuric acid (Note 5) (625–650 ml.). The acidified solution is placed in a 3-l. flask, 2 g. of zinc dust is added, and the *m*-thiocresol is distilled with steam. The lower layer of the *m*-thiocresol is separated; the aqueous layer is extracted with three 100-ml. portions of ether, the extracts being added to the oil. After drying with 50 g. of Drierite, the ether is removed by distillation, and the oily residue is distilled under reduced pressure. The yield of colorless *m*-thiocresol, b.p. 90–93°/25 mm., is 59–69 g. (63–75%) (Notes 6 and 7). It is best preserved in sealed glass bottles because of its disagreeable odor.

2. Notes

1. Eastman Kodak Company technical potassium ethyl xanthate was used.

2. The diazonium solution is left in the ice bath, and only 10 to 15-ml. portions are placed in the dropping funnel at one time.

3. Many diazonium solutions have been reported to react explosively with solutions of metallic polysulfides even at low temperatures.[1,2] A violent reaction with xanthates is mentioned only in one report.[3] Neither the authors nor the checkers observed any unusual reactivity during this preparation or with the procedure given for dithiosalicylic acid.[4] On a large scale (100 moles of *m*-toluidine) flashes of light have been occasionally observed (private communication, L. J. Roll).

4. This wash serves to remove any *m*-cresol present.

5. This acidification liberates carbon oxysulfide, which has a very disagreeable odor.

6. The refractive index is n_D^{25} 1.568–1.571.

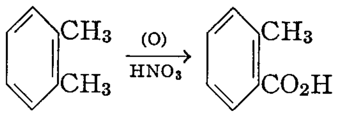
7. Other boiling points are 195°/760 mm.; 120°/100 mm.; 107°/50 mm.

3. Methods of Preparation

The only practical laboratory procedure for preparing *m*-thiocresol is by the alkaline hydrolysis of *m*-tolyl ethyl xanthate, obtained from *m*-toluenediazonium chloride and potassium ethyl xanthate.[3,5] The procedure described is essentially that of Bourgeois.[5]

[1] Nawiasky, Ebersole, and Werner, *Chem. Eng. News*, **23**, 1247 (1945).
[2] Hodgson, *Chemistry & Industry*, **1945**, 362.
[3] Leuckart, *J. prakt. Chem.*, [2] **41**, 189 (1890).
[4] *Org. Syntheses* Coll. Vol. **2**, 580 (1943).
[5] Bourgeois, *Rec. trav. chim.*, **18**, 447 (1899).

o-TOLUIC ACID



Submitted by Harold E. Zaugg and Richard T. Rapala.
Checked by R. L. Shriner and Curtis M. Snow.

1. Procedure

In a 5-l. round-bottomed flask are placed 1.6 l. of water, 800 ml. of concentrated nitric acid (sp. gr. 1.42), and 400 ml. (364 g.; 3 moles) of commercial 90% *o*-xylene (Note 1). A reflux condenser (40 cm. or longer) is fitted to the flask with a cork, and a gas absorption trap [1] is attached to the top of the condenser. The mixture is refluxed by heating in an oil bath kept between 145° and 155° for 55 hours (Note 2). At the end of this time the organic layer has settled to the bottom of the flask. The hot reaction mixture is poured with stirring into 1 kg. of ice in a 4-l. beaker. After cooling, the solid product is filtered, suspended in 2 l. of cold water, and filtered again. The wet product is dissolved by warming in 1 l. of 10% sodium hydroxide solution. After cooling, any unreacted xylene is separated by extraction with 250 ml. of ether. The aqueous layer is then heated on the steam bath with 5–10 g. of Norite and filtered hot with suction through a layer of Norite. The warm, clear red alkaline solution is added with vigorous mechanical stirring to 225 ml. of concentrated hydrochloric acid. The product is filtered from the warm solution, washed with cold water, and sucked as dry as possible on a Büchner funnel (Note 3).

The crude product is dissolved in 350 ml. of 95% ethanol and heated on the steam bath with 5 g. of Darco for 1 hour. The hot solution is filtered by gravity through a heated funnel. The filter paper is heated with an additional 70-ml. portion of 95% ethanol, and the mixture is filtered hot through a fresh paper, into the main

solution. To the alcoholic solution, adjusted to a temperature of 55–60°, is added 480 ml. of warm (55–60°) water. After being cooled first to room temperature and then to ice-bath temperature, the crystallized product is filtered, washed with 250 ml. of cold 50% ethanol, and dried (Note 4). The yield of light tan product melting at 99–101° amounts to 218–225 g. (53–55%) (Notes 5 and 6).

2. Notes

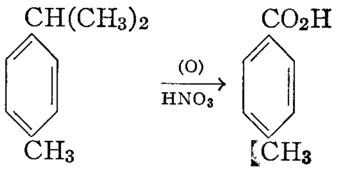
1. The *o*-xylene (90–92% purity) may be obtained from the Barrett Division of the Allied Chemical and Dye Corporation, 40 Rector Street, New York 6, New York.
2. It is not necessary that this heating be continuous. Longer times of refluxing or mechanical stirring do not improve the yield.
3. The crude product after air drying for 24–30 hours weighs between 250 g. and 300 g. and melts at 94–98°.
4. If the humidity is low, the product may be air dried; otherwise, it is best to dry in a vacuum desiccator overnight at room temperature. *o*-Toluic acid sublimes at higher temperatures.
5. The yield depends on the *o*-xylene content of the starting material. The yields stated are based on 90% *o*-xylene.
6. This product is pure enough for most purposes. Pure white needles of *o*-toluic acid may be obtained by recrystallization from water (2 l. of water for 20 g. of acid), Darco being used for decolorization. The recovery is about 85% of white needles melting at 101–103°.

3. Methods of Preparation

References to methods of preparation are given in earlier volumes.[2]

[1] *Org. Syntheses* Coll. Vol. **2**, 4 (1943).
[2] *Org. Syntheses*, **11**, 97, (1931); Coll. Vol. **2**, 589 (1943).

p-TOLUIC ACID



Submitted by W. F. Tuley and C. S. Marvel.
Checked by H. T. Clarke and D. Blumenthal

1. Procedure

In a 5-l. round-bottomed flask are mixed 2.7 l. of water and 750 ml. of concentrated nitric acid (sp. gr. 1.42). The flask is fitted with an efficient stirrer (Note 1) and a reflux condenser whose outlet is connected with a trap to remove oxides of nitrogen. One hundred and five grams (125 ml., 0.78 mole) of *p*-cymene (Note 2) is added, the stirrer is started, and the reaction mixture is boiled gently for 8 hours. It is then allowed to cool, and the solid which crystallizes is collected on a hardened filter paper in a Büchner funnel (Note 3). The crude product (Note 4) is washed with 200 ml. of water in small portions and then dissolved in 850 ml. of 1 *N* sodium hydroxide. The alkaline solution is placed in a 2-l. flask with 20 g. of zinc dust (Note 5) and distilled until the distillate runs clear (Note 6). The undissolved zinc is removed by filtration, and the yellowish filtrate is poured in a thin stream with vigorous stirring into 500 ml. of boiling 5 *N* hydrochloric acid. After cooling, the precipitated acid is filtered, washed with cold water until substantially free of chloride, and dried. About 80 g. of a light brown powder is thus obtained.

The product is extracted for 6 hours with 300 ml. of toluene in the apparatus described in a previous volume [1] (Note 7). The toluene extract is chilled to 0°, and the light brown crystals of *p*-toluic acid are filtered. This material weighs 56–58 g.; an additional 5 g. is obtained by concentrating the filtrate to 100 ml.

The total yield of product melting at 174–177° is 60–63 g. (56–59%). The acid may be purified further with very little loss by dissolving it in 0.5 *N* sodium hydroxide, treating the solution with Norite, precipitating the acid by pouring the alkaline solution into excess hot hydrochloric acid, and recrystallizing the product from toluene (Note 8). The purified *p*-toluic acid melts at 176–177° and weighs about 55 g. (51%).

2. Notes

1. A stirrer of the tubular type, running in a bearing consisting of a glass tube which extends well below the surface of the liquid, is recommended.
2. The fraction of spruce turpentine which boils at 175–178° is satisfactory.
3. The filtrate contains too little dissolved product (about 4 g.) to repay extraction. It can be employed for a subsequent run by adding sufficient concentrated nitric acid (*ca.* 300 ml.) to restore the specific gravity to its initial value, 1.115.
4. The crude product consists of *p*-toluic acid contaminated with small amounts of terephthalic acid, methyl *p*-tolyl ketone, and nitration products.
5. The zinc serves to reduce nitration products that are otherwise difficult to remove. The resulting amines remain in the filtrate after acidification.
6. About 300 ml. of distillate is collected, of which 5 ml. consists of methyl *p*-tolyl ketone.
7. About 4 g. of light tan terephthalic acid remains on the filter paper.
8. The last traces of color are removed only with considerable difficulty by Norite. An alternative procedure consists in distilling the toluic acid under reduced pressure from a two-bulbed flask with a wide connecting tube [2] and crystallizing the distillate from toluene.

3. Methods of Preparation

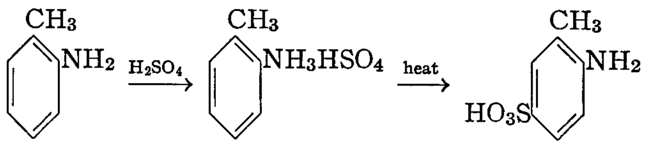
p-Toluic acid has been prepared by the oxidation of cymene,[3] *p*-xylene,[4] or dihydro-*p*-tolualdehyde [5] with nitric acid; by the

reaction between *p*-chlorotoluene and metallic sodium [6] or butyllithium [7] followed by carbonation; by the hydrolysis of *p*-tolunitrile; [8] and by fusing phenyl *p*-tolyl ketone or di-*p*-tolyl ketone with potassium hydroxide.[9]

[1] *Org. Syntheses* Coll. Vol. **1**, 375 (1941).
[2] *Org. Syntheses*, **20**, 20 (1940).
[3] Noad, *Ann.*, **63**, 287 (1847).
[4] Yssel de Schepper and Beilstein, *Ann.*, **137**, 302 (1866).
[5] Allen, Ball, and Young, *Can. J. Research*, **9**, 169 (1933).
[6] Morton, LeFevre, and Hechenbleikner, *J. Am. Chem. Soc.*, **58**, 754 (1936).
[7] Gilman, Wright, and Moore, *J. Am. Chem. Soc.*, **62**, 2330 (1940).
[8] *Org. Syntheses* Coll. Vol. **2**, 589 (1943).
[9] Kozlov, Fedoseev, and Lazarev, *J. Gen. Chem. U.S.S.R.*, **6**, 485 (1936) [*C. A.*, **30**, 5574 (1936)].

o-TOLUIDINESULFONIC ACID

(*m*-Toluenesulfonic acid, 6-amino-)



Submitted by C. F. H. Allen and J. A. VanAllan.
Checked by R. L. Shriner and Charles R. Russell.

1. Procedure

In a 500-ml. three-necked round-bottomed flask, fitted with a stirrer, thermometer, and 250-ml. dropping funnel, are placed 19 ml. of water and 27.8 ml. (0.5 mole) of concentrated sulfuric acid (sp. gr. 1.84), and the whole is warmed to 70°. From the dropping funnel is added, dropwise, over a 0.5-hour period, 53.5 g. (0.5 mole) of *o*-toluidine (Note 1). The temperature is allowed to reach about 85° in order to prevent the separation of solid before all the amine has been added. When addition is complete, the temperature is raised to 100–105° for 5 minutes. The flask is then placed on a steam bath, the stirrer and dropping

funnel are removed, and the flask is evacuated by means of a water pump to about 15 mm. (Note 2); after 21 hours all the water has been removed. The flask is then immersed in an oil bath, and the internal temperature is raised to 180° over a period of 2 hours and kept at 180–195° (bath temperature about 190–205°) for 7 hours while the same diminished pressure is maintained (Note 3). The crude product is dissolved in 1.3 l. of boiling water, and 99 g. of barium hydroxide octahydrate is added with stirring; the solution is now alkaline to litmus. After the addition of 3 g. of Norite, the solution is heated for 1.5 hours on a steam bath, and 17.5 ml. of concentrated sulfuric acid (sp. gr. 1.84) diluted with 20 ml. of water is added with good stirring. The solution is heated to 96° and filtered through a large, preheated Büchner funnel; the filter cake is rinsed with 100 ml. of boiling water (Note 4).

The filtrate is transferred to a 3-l. round-bottomed flask and concentrated under a pressure of about 50 mm. to a volume of 200 ml. (Note 5). After the mixture has been chilled overnight in a refrigerator, the crystalline acid (68–74 g.) is filtered by suction and dried (Note 6). An additional small amount (5–8 g.) can be obtained by evaporating the filtrate to dryness. This residue is allowed to remain in contact with 75 ml. of methanol for about an hour with occasional shaking. The solid is filtered, dried, and weighed. The total yield of *o*-toluidinesulfonic acid is 74–79 g. (79–83%) (Notes 7 and 8).

2. Notes

1. The amine used should boil over a range of not more than 2°.

2. If time is an important consideration, and a smaller yield (60%) is acceptable, the procedure may be modified: the acid sulfate is heated for 1 hour under reduced pressure; the temperature is then raised to 180° for 1 hour and finally to 180–190° for 3 hours. The solid residue is taken up in 1 l. of hot water and 55 ml. of 40% sodium hydroxide, a small amount of unchanged amine is distilled with steam, and the clear solution is treated with

Norite and filtered as above. The acid is then precipitated by adding 65 ml. of concentrated hydrochloric acid.

3. During this time the amine acid sulfate melts and loses water, and the product solidifies to a white crystalline mass.

4. Low yields may result from crystallization of some of the acid in the funnel at this point if the funnel is preheated insufficiently. Some acid may also be lost in the large bulk of inorganic solid. Filtration through the finely divided filter cake is often so slow that the under side and stem of the funnel collect large amounts of crystalline acid which is not rinsed out by the 100 ml. of boiling water. The use of a steam-heated Büchner funnel or prolonged preheating of an ordinary Büchner funnel does not seem to minimize this effect. It is advisable to remove the funnel after filtration is complete, and to take out the filter cake and rinse the funnel with two 100-ml. portions of boiling water. The combined washings are heated to boiling and filtered, and the filtrate is added to that obtained in the original filtration.

5. The flask should be equipped with a still head to prevent carry-over of the solution during distillation; a capillary jet is also an aid in this evaporation. Much of the acid separates during this concentration; the crystals are easily filterable.

6. The acid was spread out on a large filter paper and dried above a steam radiator for 48 hours. The literature reports the acid to be a monohydrate which loses its water of crystallization by drying at 120° for 3 hours. However, titration of the air-dried acid showed that it was not hydrated. A sample of the acid heated to 120° for 3 hours showed no change in neutral equivalent.

7. This aminosulfonic acid has no definite melting point. On a Maquenne block a decomposition range of 335–380° was observed.

8. The product secured by this procedure is free from sodium sulfate and isomeric sulfonic acids. Titrations of the first crop of crystals gave neutral equivalents ranging from 187.0 to 187.6; the calculated neutral equivalent is 187.2. The second crop is less pure since it had a neutral equivalent of about 177.

3. Methods of Preparation

o-Toluidinesulfonic acid has been obtained by a variety of reactions. Of these the ones of preparative value are the sulfonation of *o*-toluidine by fuming sulfuric acid;[1,2,3] the rearrangement of the amine sulfate or acid sulfate;[4,5] and the reduction of the corresponding nitrotoluenesulfonic acid.[6] The above procedure is based on the directions of Huber,[5] who has described the preparation of ten aminoarylsulfonic acids by this method.

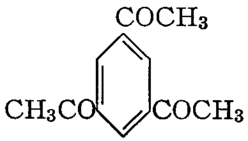
[1] Gerver, *Ann.*, **169**, 374 (1873).
[2] Claus and Immel, *Ann.*, **265**, 72 (1891).
[3] Schultz and Lucas, *J. Am. Chem. Soc.*, **49**, 299 (1927).
[4] Neville and Winther, *Ber.*, **13**, 1941 (1880).
[5] Huber, *Helv. Chim. Acta*, **15**, 1372 (1932).
[6] Foth, *Ann.*, **230**, 306 (1885).

1,3,5-TRIACETYLBENZENE

(Benzene, 1,3,5-triacetyl)

$$HCO_2C_2H_5 + CH_3COCH_3 + NaOC_2H_5 \rightarrow CH_3COCH{=}CH(ONa) + 2C_2H_5OH$$

$$3CH_3COCH{=}CH(ONa) + 3CH_3CO_2H \rightarrow$$



$$+ 3CH_3CO_2Na + 3H_2O$$

Submitted by Robert L. Frank and Robert H. Varland.
Checked by Arthur C. Cope and W. H. Jones.

1. Procedure

Sixty-nine grams (3.0 gram atoms) of freshly cut sodium is placed in a 1-l. round-bottomed flask with 400 ml. of dry xylene (Note 1) and heated until all the sodium is melted. The flask is closed with a rubber stopper and shaken vigorously to form finely powdered sodium (Note 2). When cool, the contents are

transferred to a 5-l. three-necked round-bottomed flask, and the xylene is decanted. The powdered sodium is then washed with two 100-ml. portions of anhydrous ether by decantation, after which 1 l. of anhydrous ether is added. The flask is placed on a steam bath and fitted with a Hershberg stirrer, an upright condenser, and a 500-ml. dropping funnel. The condenser and funnel are protected from moisture by calcium chloride tubes. Through the dropping funnel is then added with stirring 138 g. (175 ml., 3.0 moles) of absolute alcohol at such a rate that gentle refluxing occurs. The mixture is refluxed and stirred for 6 hours after the addition is complete.

The reaction mixture is diluted with 1.5 l. of anhydrous ether, and a mixture of 174 g. (220 ml., 3.0 moles) of acetone (Note 3) and 222 g. (241 ml., 3.0 moles) of ethyl formate (Note 4) is placed in the dropping funnel and added to the flask over a period of 2 hours. Stirring is continued for 2 hours after the acetone and ethyl formate have been added (Note 5).

The reaction mixture is then rapidly extracted with five 1-l. portions of water (Note 6). Acetic acid is added to the water solution until it is acid to litmus. The acidified solution is warmed to 50° on a steam bath and maintained at approximately that temperature for 2 hours. It is subsequently allowed to stand at room temperature for 48 hours, during which time the triacetylbenzene crystallizes.

The crude yellow crystalline solid (m.p. in the range 150–162°) is collected on a filter; the yield is 84–94 g. (41–46%). It is recrystallized by dissolving in hot alcohol (18 ml. of alcohol per gram), adding 2 g. of Norite, filtering through a steam-heated funnel (Note 7), and cooling the filtrate in an ice bath. The yield of shiny white crystals, m.p. 162–163°, is 62–79 g. (30–38%) (Note 8).

2. Notes

1. The first portion of this synthesis is very similar to the preparation of acetylacetone by the method of Adkins and Rainey.[1] The procedure and Notes 1–6 and 8 for that synthesis may therefore be helpful in the present preparation.

2. A more finely powdered sodium can be obtained if paraffin oil ("Stanolind") is used in place of xylene (Gilbert Ashburn, private communication).

3. Acetone dried over calcium sulfate and distilled from phosphorus pentoxide is satisfactory.

4. The ethyl formate is dried over calcium sulfate and distilled.

5. If the solution becomes so thick as to make stirring difficult, it is advisable to add more anhydrous ether.

6. It is important that the extraction and acidification be carried out without delay. Oxidation of the intermediate product takes place readily on exposure to air and causes the solution to become dark in color.

7. If a steam-heated funnel is not used, a larger volume of alcohol should be employed to prevent crystallization during filtration.

8. The higher yield (38%) was obtained if the commercial absolute alcohol was dried by treatment with sodium and ethyl phthalate.[2]

3. Method of Preparation

Triacetylbenzene has been prepared only by the condensation of acetone with ethyl formate followed by the trimerization of the intermediate acetylacetaldehyde.[3,4]

[1] *Org. Syntheses*, **20**, 7 (1940).
[2] *Org. Syntheses* Coll. Vol. **2**, 155 (1943).
[3] Claisen and Stylos, *Ber.*, **21**, 1145 (1888).
[4] Kaushal, Sovani, and Deshapande, *J. Indian Chem. Soc.*, **19**, 107 (1942).

SUBJECT INDEX

(This cumulative index comprises material from Volumes 20 *through* 27 *of this series; for previous volumes see Collective Volumes* 1 *and* 2.)

Names in small capital letters refer to the titles of individual preparations. A number in ordinary bold-face type denotes the volume. A number in bold-face italics refers to a page which gives preparative directions for substances formed either as principal products or as by-products; numbers in ordinary type indicate pages on which a compound or a subject is mentioned in connection with other preparations. For example, Acetone cyanohydrin, **20**, 42, ***43***, indicates that acetone cyanohydrin is mentioned on page 42, and that directions for its preparation are given in detail on page 43, of Volume 20.

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